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DFT Study of Aromatization on Azo-Linked Cyclopentadienides

M. Moayeri, M. Nikpassand*
Department of Chemistry, Rasht Branch, Islamic Azad University, P. O. Box: 3516-41335, Rasht, Iran.

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ABSTRACT

The aromatic behavior of the azo-linked cyclopentadienide derivatives have been revealed in various natural compounds. In this research, density functional theory (DFT) calculations at the B3LYP level are used to optimize the geometry of the compounds. In addition, we were interested in the evaluation of the aromaticity of the selected compounds using nucleus independent chemical shifts NICS (0), NICS (0.5), NICS (1), NICS (1.5) and NICS (2), bond lengths and bond angles. Prog. Color Colorants Coat. 14 (2021), 13-26© Institute for Color Science and Technology.

1. Introduction

Cyclopentadienides, and their derivatives, in particular, have shown several aromatic properties. The η^5-cyclopentadienyl anion (Cp) is a famous ligand and is used extensively in organometallic chemistry. Complexes containing this ligand exist for all the transition metals and many of the f-block metals [1-3]. Computational chemistry is an important part of chemistry which studies the properties of compounds, their reactions and the optimization of existing chemical methods by using advanced and specialized softwares. The index of nuclear independent chemical shift (NICS) is one the most famous criteria, which was proposed by Schleyer et al. in 1996 for the first time and which has received attention from many chemists [4]. By this method we can measure magnetic flux in hypothetical points in the center of molecule and at different distances from it, in a way that at the distance 1Å upper than the middle of the ring, the effects of the σ bond decreases in the molecule. In addition, by this method we can better analyze the effects of π unstable electrons under field effect. This criterion has been used for justifying the aromatic property of many systems [5-10].

Aromatic compounds are named according to the number of saturated linkages they contain; mono for one interruption, etc. Three types of aromatic interactions exist: through-bond, through-space, and transannular. The best established aromatic molecules are cationic in nature, and only recently have their anionic counterparts been identified as aromatic. A truly neutral aromatic has eluded researchers thus far. The focus of this report will be to review recent efforts towards the synthesis and characterization of neutral and anionic aromatic compounds [10, 11]. Homoaromatic compounds are named according to the number of saturated linkages they contain mono for one interruption etc. such as cycloheptatriene [12] and dihydro-1,2,4,5-tetrazine [13]. Three types of homoaromatic interactions exist: through-bond, through-space, and transannular. The best established homoaromatic molecules are cationic in nature, and only recently have anionic counterparts been identified as homoaromatic. A truly neutral homoaromatic structure has eluded researchers thus far. The focus of this report will be to review recent efforts towards the synthesis and

*Corresponding author: nikpassand@iaurasht.ac.ir

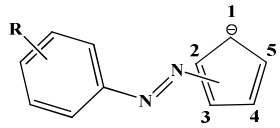
characterization of neutral and anionic homoaromatic compounds [11, 12].

2. Results and Discussion

All theoretical calculations were performed using the Gaussian 09W program package [12] without any constraint on the geometry. Seventy-two possible structures of azo-linked heterocycles were fully optimized at the B3LYP level, using 6-311G++(d) basis set.

The main purpose of this research is to calculate density functional theory (DFT) at the B3LYP level of those cyclopentadienide compounds which have aryl azo bridge in order to study the effects of these bridges on the extent of the aromatic property of these compounds. For this reason, first, all these structures (Figure 1) have been optimized by using the Gaussian 2009 software (Table 1) and the index of nuclear independent chemical shift (NICS) (Tables 1 and 2) and subsequently the bond lengths (Angstrom) and also some of the bond angles (Table 3) in the intended compounds were evaluated.

All theoretical calculations were performed using the Gaussian 09W program package [12] without any constraint on the geometry. Ninety possible structures of azo-linked heterocycles were fully optimized.



R= H, CH_3, OCH_3, NH_2, NO_2, Cl

Figure 1: Formula of azo-linked cyclopentadienides 1-72.

Table 1: Calculated total energy and NICS indexes of azo-linked cyclopentadienides.

Compound	R	Azo linked site	Total Energy (Hart./particles)	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	NICS(2)
1	H	1	-534.188963465	-3.0723	-4.9361	-6.4759	-5.0991	-3.1228
2	3-CH_3	1	-573.513100338	-3.1908	-5.0733	-6.5792	-5.1320	-3.1243
3	4-CH_3	1	-738.772398858	-3.4102	-5.0800	-6.1612	-4.8020	-3.0279
4	2-NO_2	1	-738.750759661	-3.9432	-5.3598	-6.2741	-4.7843	-2.9464
5	3-NO_2	1	-738.762106604	-4.8176	-6.3067	-7.0353	-5.1992	-3.0942
6	4-NO_2	1	-738.772398858	-3.8218	-5.4135	-2.3917	-4.8380	-2.9288
7	2-CH_3O	1	-648.730468536	-5.0626	-6.5763	-7.1508	-5.0460	-2.8911
8	3-CH_3O	1	-648738914568	-3.1444	-5.0058	-6.5048	-5.0733	-3.0860
9	4-CH_3O	1	-648.737150481	-4.2444	-5.8199	-6.6774	-5.1069	-3.1946
10	2-Cl	1	-993.814707449	-3.5913	-5.1646	-6.3364	-4.9012	-2.9957
11	3-Cl	1	-648.738914568	-6.5450	-8.4725	-8.6657	-5.6903	-3.2086
12	4-Cl	1	-993.820533594	-3.8913	-5.4379	-6.3816	-4.8268	-2.9238
13	H	2	-534.188459802	-2.9048	-4.2036	-4.8709	-3.2846	-2.6509
14	3-CH_3	2	-573.513209467	-2.0962	-4.2057	-4.8726	-4.3287	-3.0054
15	4-CH_3	2	-738.772309764	-3.0591	-3.9380	-5.2904	-4.0657	-3.0423
16	2-NO_2	2	-738.750761964	-2.2984	-3.8605	-4.5489	-4.0267	-2.0917
17	3-NO_2	2	-738.762321943	-4.1936	-5.7935	-3.3267	-3.8240	-3.0923
18	4-NO_2	2	-738.772383077	-3.2195	-5.0276	-2.9370	-4.0163	-2.2904

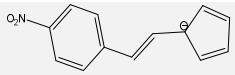
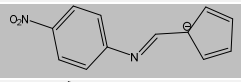
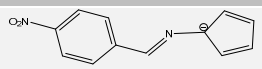
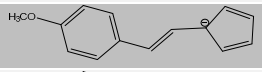
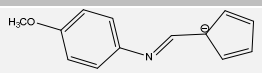
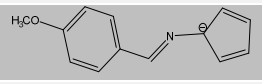
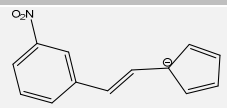
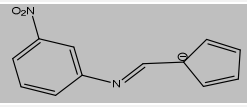
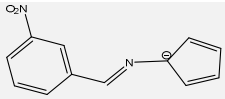
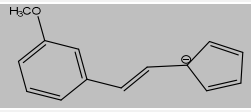
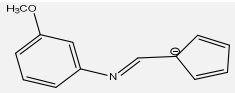
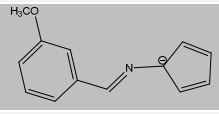
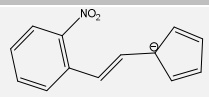
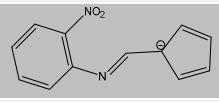
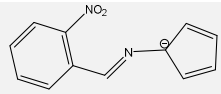
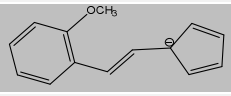
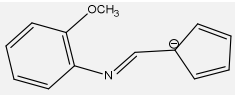
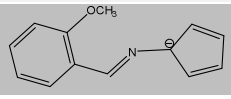
Table 1: Continue.

Compound	R	Azo linked site	Total Energy (Hart./particles)	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	NICS(2)
19	2-CH_3O	2	-648.730465870	-5.0006	-4.8604	-5.8046	-5.0058	-2.0272
20	3-CH_3O	2	-648.738903879	-3.0482	-4.0050	-6.5048	-5.0743	-3.0837
21	4-CH_3O	2	-648.737139829	-4.2476	-5.8121	-5.6765	-4.1041	-3.1054
22	2-Cl	2	-993.814720964	-2.9740	-4.2702	-5.7892	-4.0480	-2.1562
23	3-Cl	2	-648.738920917	-5.3267	-6.2675	-5.3703	-4.7218	-3.4105
24	4-Cl	2	-993.820543198	-3.4295	-3.8046	-4.0176	-4.0373	-2.4384
25	H	3	-534.188895048	-3.0973	-4.0040	-5.6538	-5.1047	-3.1331
26	3-CH_3	3	-573.513205890	-3.0370	-5.1874	-4.0582	-4.0046	-3.0056
27	4-CH_3	3	-738.772096554	-3.2190	-5.0674	-6.2187	-4.6290	-3.1183
28	2-NO_2	3	-738.750750953	-3.6521	-5.0435	-6.8739	-4.5418	-2.2189
29	3-NO_2	3	-738.762209147	-4.0451	-6.2890	-7.0032	-5.0342	-3.0065
30	4-NO_2	3	-738.772387609	-4.8945	-4.4623	-2.7830	-3.9063	-3.5498
31	2-CH_3O	3	-648.730390653	-5.3251	-5.8679	-4.3280	-4.3257	-2.7904
32	3-CH_3O	3	-648.738920954	-3.4728	-5.8204	-5.0943	-4.1734	-3.2410
33	4-CH_3O	3	-648.737209742	-3.8732	-4.0473	-4.0352	-5.0341	-3.0054
34	2-Cl	3	-993.814716509	-3.1974	-5.287	-5.3245	-4.0925	-2.4398
35	3-Cl	3	-648.738920964	-5.1093	-5.8790	-6.2930	-5.0927	-3.5497
36	4-Cl	3	-993.820534389	-3.3298	-5.6750	-5.8836	-4.9305	-2.8745
37	2-NO_2 and 2´-NO_2	1 and 2	-1283.92767602	11.0935–	-10.0346	5.3811–	3.1495–	0.9231–
38	2-NO_2 and 2´-NO_2	1 and 3	-1283.92975320	11.9546–	-10.9057	5.7351–	2.9636–	0.2397–
39	2-NO_2 and 2´-NO_2	1 and 4	-1283.93085429	11.3510–	-10.6328	5.0376–	3.5152–	1.3066–
40	3-NO_2 and 3´-NO_2	1 and 2	-1283.92870935	12.9731–	-10.9702	5.9763–	3.5498–	102145–
41	3-NO_2 and 3´-NO_2	1 and 3	-1283.92095658	12.976–	-10.9804	5.7600–	2.9914–	1.7845–
42	3-NO_2 and 3´-NO_2	1 and 4	-1283.93206576	12.0356–	-10.8309	5.3572–	3.3830–	1.7503–
43	4-NO_2 and 4´-NO_2	1 and 2	-1283.92938408	12.9330–	-10.9123	5.9763–	3.5490–	1.0934–
44	4-NO_2 and 4´-NO_2	1 and 3	-1283.93950356	12.9730–	-10.9502	5.6502–	2.7605–	2.2315–
45	4-NO_2 and 4´-NO_2	1 and 4	-1283.93956438	12.8921–	-10.6903	5.6090–	3.2135–	1.3279–
46	2-CH_3O and 2´-CH_3O	1 and 2	-1103.88037320	11.3769–	7.2195–	5.1904–	1.7652–	-0.6925
47	2-CH_3O and 2´-CH_3O	1 and 3	-1103.88036953	11.1309–	6.8700–	5.2404–	1.4980–	-0.8252
48	2-CH_3O and 2´-CH_3O	1 and 4	-1103.87092843	11.4350–	6.3875–	5.5596–	1.1865–	-0.6104

Table 1: Continue.

Compound	R	Azo linked site	Total Energy (Hart./particles)	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	NICS(2)
49	3-CH_3O and 3´-CH_3O	1 and 2	-1103.88038320	11.0436-	8.9365-	5.0843-	1.7560-	-1.0464
50	3-CH_3O and 3´-CH_3O	1 and 3	-1103.87929836	11.2180-	6.8947-	5.5904-	1.9031-	-0.8140
51	3-CH_3O and 3´-CH_3O	1 and 4	-1103.89795162	11.1690-	6.8184-	5.8460-	1.1843-	-0.8152
52	4-CH_3O and 4´-CH_3O	1 and 2	-1103.88072311	12.6588-	8.9898-	5.0843-	1.4565-	-0.9803
53	4-CH_3O and 4´-CH_3O	1 and 3	-1103.88051168	12.0937-	6.3800-	5.4380-	1.8209-	-0.7603
54	4-CH_3O and 4´-CH_3O	1 and 4	-1103.88201467	11.3206-	6.9797-	5.5709-	1.0265-	-0.5793
55	H	2 and 5	-874.799559977	-11.5707	10.0299-	5.2134-	-1.8848	0.6906-
56	4-CH_3 and 4´-CH_3	2 and 5	-953.448477478	11.0237-	9.4820-	4.8074-	-1.6536	0.5642-
57	4-NO_2 and 4´-NO_2	2 and 5	-1283.94626193	12.1621-	-10.4221	5.4090-	1.9835-	0.7301-
58	4-CH_3O and 4´-CH_3O	2 and 5	-1103.89814920	10.2817-	8.7419-	4.2556-	1.3438-	-0.4046
59	4-Cl and 4´-Cl	2 and 5	-1794.05722713	-11.4385	-9.8461	5.0382-	-1.7612	0.6020-
60	3-CH_3 and 3´-CH_3	2 and 5	-953.448907198	-11.3694	8.9792-	-3.3571	0.9349-	-0.2602
61	3-NO_2 and 3´-NO_2	2 and 5	-1283.93499514	-12.7925	-11.2140	6.0858-	2.3702-	0.9364-
62	3-CH_3O and 3´-CH_3O	2 and 5	-1103.90210698	11.3505-	-8.5249	-2.7480	0.7023-	0.1479-
63	3-Cl and 3´-Cl	2 and 5	-1794.05727117	11.9965-	-10.4056	5.4536-	0.9924-	0.7225-
64	H	3 and 4	-874.788984411	-22.8450	21.7525-	14.4641-	7.1822-	3.5139-
65	4-CH_3 and 4´-CH_3	3 and 4	-953.437901949	22.1326-	21.0145-	13.9043-	6.8584-	3.3475-
66	4-NO_2 and 4´-NO_2	3 and 4	-1283.93682164	22.8601-	21.3801-	13.9499-	6.8584-	3.3374-
67	4-CH_3O and 4´-CH_3O	3 and 4	-1103.88773042	-21.0064	19.8348-	12.9976-	6.3589-	-3.0833
68	4-Cl and 4´-Cl	3 and 4	-1794.04743312	22.5346-	21.3183-	14.0439-	6.9110-	3.3496-
69	3-CH_3 and 3´-CH_3	3 and 4	-953.438233260	-2.9539	-5.3171	-5.4656	-3.7491	-2.1083
70	3-NO_2 and 3´-NO_2	3 and 4	-1283.92658305	-2.6985	-5.0890	-5.3495	-3.7191	-2.1031
71	3-CH_3O and 3´-CH_3O	3 and 4	-1103.89145043	-2.9302	-5.2286	-5.3762	-3.7014	-2.0924
72	3-Cl and 3´-Cl	3 and 4	-1794.04780436	-3.2076	-5.0102	-5.5635	-4.1996	-2.5005

Table 2: Calculated total energy and NICS indexes of some vinyl and imine-linked cyclopentadienides.

Compound	structure	Total Energy (Hart./particles)	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	NICS(2)
73		-706.69957728	-3.9585	-5.5934	-6.5700	-5.0827	-3.2063
74		-722.75119431	-3.5918	-5.2672	-6.3065	-4.9032	-3.0933
75		-722.74319455	-3.9879	-5.6651	-6.6937	-5.1759	-3.2553
76		-616.66066711	-5.0577	-7.0372	-6.1195	-3.1607	-1.5780
77		-632.71656091	-5.4825	-12.6397	-3.5815	-0.9301	-0.4915
78		-632.70733609	-5.2592	-7.3694	-6.3568	-3.2748	-1.6413
79		-706.68637390	-4.4369	-5.9814	-6.7783	-5.1895	-3.2647
80		-722.74001877	-4.3149	-5.8716	-6.6933	-5.1211	-3.2090
81		-722.73197107	-4.5866	-6.2090	-7.0340	-5.3692	-3.3722
82		-616.66372666	-5.0272	-6.6486	-6.8666	-4.3576	-2.3538
83		-632.71874787	-5.4252	-6.8629	-7.5687	-5.6023	-3.3475
84		-632.70944862	-5.1020	-6.7055	-7.1787	-4.7975	-2.6734
85		-706.68369177	-3.9752	-5.4824	-6.5834	-5.0843	-3.1393
86		-722.73110527	-4.8098	-8.5288	-14.498	-10.8639	-4.8969
87		-722.79935098	-4.1480	-6.2264	-6.4571	-3.6904	-2.1462
88		-616.65975028	-4.7413	-6.1963	-7.0211	-5.2958	-3.2041
89		-632.71118841	-5.3647	-7.4459	-9.3707	-6.9476	-3.7836
90		-632.70534118	-5.0426	-6.5282	-7.3219	-5.4822	-3.3003

In view of this and in continuation of our efforts for the preparation and theoretical study of azo-linked compounds [13-21], we probed to study a number of cyclopentadienide structures with different aryl azo linkages. The basis of the selection of this series of compounds is to analyze the existence of aromatic property in these compounds from an overall perspective such as analyzing bond length and bond angel in compounds and analyzing the NICS of some of them based on position, type or frequency of aryl azo linkages or substitution of phenyl in cyclopentadienides.

2.1. Results of comparing magnetic behavior of some molecules based on the position of aryl azo linkages in cyclopentadienides

The study of the effect of the same aryl azo linkages at different positions of cyclopentadienide showed that the 4-methoxy aryl azo linkage has an electron withdrawing field effect at position 1 but shows a donor resonance effect at positions 2 and 3 of cyclopentadienide ring. On the other hand, the results of aryl azo substitutions with 4-nitro group have close values of NICS at positions 1, 2 or 3 (Figure 2). The results in diagrams C and D in Figure 2 indicate that cyclopentadienide consists of two aryl azo substitutions (bis-aryl azo cyclopentadienide) with the nitro or methoxy group, and has close values of NICS at different position rings and their fluctuation is low (Figure 2). It seems that the existence of each substitution at positions 3 and 4 in bis-aryl azo cyclopentadienides yields the best values of NICS.

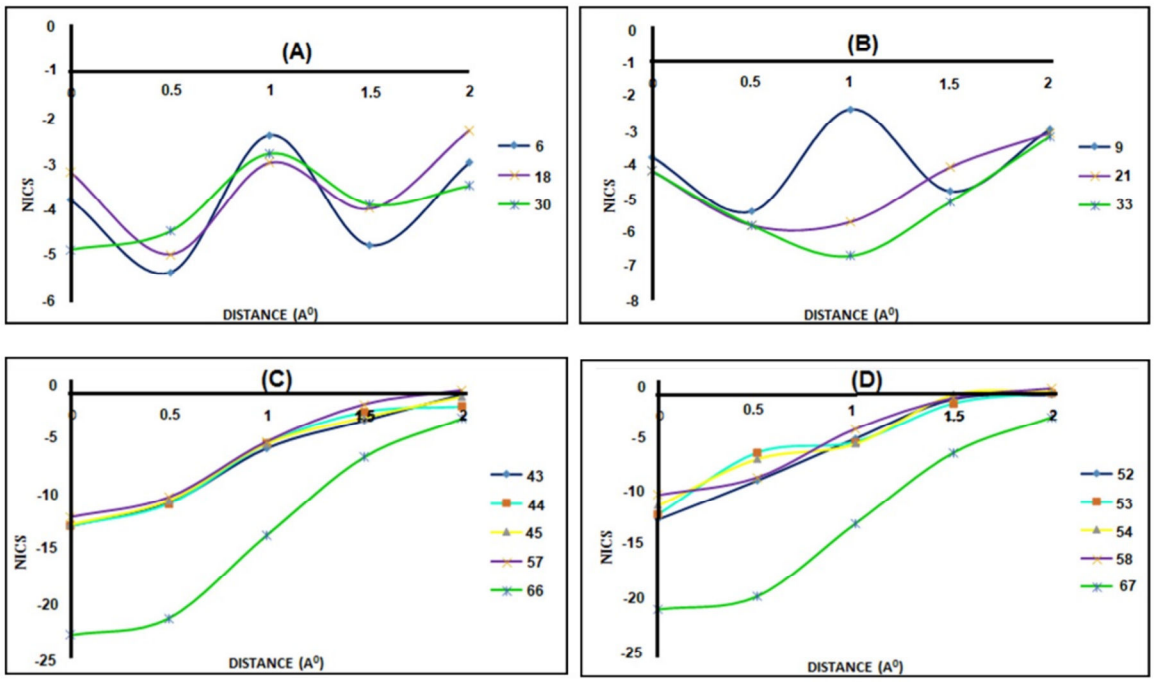


Figure 2: Comparing magnetic behavior of some molecules based on the position of aryl azo linkages in cyclopentadienides.

Table 3: Some of calculated bond lengths (Angstrom) and bond angles of azo-linked cyclopentadienides.

Compound	C_1-C_2	C_2-C_3	C_3-C_4	C_1-C_2-C_3	C_2-C_1-C_5
1	1.4322	1.4984	1.4845	118.8474	119.4517
2	1.4342	1.4922	1.4780	118.6732	119.6133
3	1.4385	1.4913	1.4751	118.6342	119.5873
4	1.4288	1.4864	1.4765	118.6044	119.5336
5	1.4343	1.4834	1.4787	118.5647	119.4908
6	1.4357	1.4835	1.4775	118.8119	119.6860
7	1.4231	1.4844	1.4791	118.7114	119.6400
8	1.4435	1.4991	1.4745	120.1809	119.8392
9	1.4420	1.4983	1.4734	120.1562	119.8419
10	1.4439	1.4972	1.4727	120.1312	119.8661
11	1.4644	1.4963	1.4713	120.0573	119.8815
12	1.4653	1.4026	1.4754	120.4524	118.9322
13	1.4615	1.4995	1.4743	120.4507	118.8584
14	1.4567	1.4933	1.4826	118.0001	118.4539
15	1.4275	1.4933	1.7553	119.9798	118.4524
16	1.4479	1.4931	1.4743	119.9936	118.4552
17	1.4546	1.4926	1.4762	118.0434	118.4692
18	1.4544	1.4945	1.4752	119.9823	118.4957
19	1.4275	1.4935	1.4763	119.9564	118.4591
20	1.4069	1.4860	1.4775	119.1553	118.9286
21	1.4439	1.4854	1.4774	119.1397	118.8917
22	1.4541	1.4844	1.4701	119.1162	118.8471
23	1.4534	1.4733	1.4760	119.0839	118.7632
24	1.4259	1.4891	1.4776	119.4223	118.1248
25	1.4260	1.4862	1.4695	119.1699	118.9799
26	1.4245	1.4864	1.4725	118.7573	118.6999
27	1.4358	1.4872	1.4674	118.7105	118.9318
28	1.4304	1.4714	1.4654	119.4162	118.0691
29	1.4246	1.4820	1.4645	119.9732	118.9151
30	1.4314	1.4733	1.4656	120.0307	118.9075

Table 3: Continue.

Compound	C_1-C_2	C_2-C_3	C_3-C_4	C_1-C_2-C_3	C_2-C_1-C_5
31	1.4512	1.4782	1.4615	120.4997	118.0701
32	1.4312	1.4761	1.4766	119.1877	118.8129
33	1.4314	1.4760	1.4717	119.1687	118.8437
34	1.4463	1.4792	1.4777	119.0859	118.0175
35	1.4365	1.4822	1.4536	119.8622	118.4384
36	1.4302	1.4730	1.4635	119.8914	118.4831
37	1.4515	1.4832	1.4665	120.4399	118.6471
38	1.4409	1.4880	1.4636	119.7423	118.8988
39	1.4352	1.4853	1.4208	119.7324	118.9051
40	1.4349	1.4993	1.4628	119.5982	118.1717
41	1.4432	1.4834	1.4597	119.8474	118.6997
42	1.4504	1.4703	1.4585	119.6732	118.4877
43	1.4440	1.4920	1.4646	119.6342	118.7037
44	1.4635	1.4995	1.4524	119.6044	118.0348
45	1.4393	1.4882	1.4675	119.5647	118.4591
46	1.4474	1.4873	1.4636	119.8119	118.9286
47	1.4630	1.4881	1.4665	119.7114	118.8917
48	1.4414	1.4882	1.4637	120.1809	118.8471
49	1.4342	1.4882	1.4546	120.1562	118.7632
50	1.4358	1.4835	1.4638	120.1312	118.1248
51	1.4404	1.4843	1.4635	120.0573	118.9799
52	1.4630	1.4792	1.4656	120.4524	118.6999
53	1.4616	1.4886	1.4687	120.4507	118.9318
54	1.4516	1.4973	1.4669	118.0001	118.0691
55	1.4317	1.4865	1.4616	119.9798	118.9151
56	1.4414	1.4820	1.4765	119.9936	118.9075
57	1.4560	1.4994	1.4715	118.0434	118.0701
58	1.4491	1.4733	1.4734	119.9823	118.8129
59	1.4274	1.4832	1.4782	119.9564	118.8437
60	1.4294	1.4731	1.4733	119.1553	118.0175

Table 3: Continue.

Compound	C_1-C_2	C_2-C_3	C_3-C_4	C_1-C_2-C_3	C_2-C_1-C_5
61	1.4474	1.4825	1.4764	119.1397	118.4384
62	1.4036	1.4945	1.4703	119.1162	118.4831
63	1.4414	1.4833	1.4754	119.0839	118.6471
64	1.4445	1.4763	1.4743	119.4223	118.8988
65	1.4553	1.4754	1.4763	119.1699	118.9351
66	1.4604	1.4845	1.4705	118.7573	118.1717
67	1.4635	1.4735	1.4716	118.7105	118.6997
68	1.4616	1.4791	1.4565	119.4162	118.4877
69	1.4513	1.4761	1.4634	119.9732	118.7037
70	1.4517	1.4767	1.4526	120.0307	118.0348
71	1.4414	1.4772	1.4734	120.4997	118.4591
72	1.4368	1.4712	1.4778	119.1877	118.9286
73	1.4596	1.4720	1.4750	119.1687	118.8917
74	1.4674	1.4831	1.4746	119.0859	118.8471
75	1.4536	1.4787	1.4769	119.8622	118.7632
76	1.4536	1.4963	1.4617	119.8914	118.1248
77	1.4614	1.4765	1.4700	120.4399	118.9799
78	1.4745	1.4998	1.4615	119.7423	118.6999
79	1.4455	1.4820	1.4634	119.7324	118.9318
80	1.4404	1.4830	1.4610	119.5982	118.0691
81	1.4635	1.4784	1.4634	118.8474	118.9151
82	1.4616	1.4880	1.4645	118.6732	118.9075
83	1.4345	1.4755	1.4606	118.6342	118.0701
84	1.4355	1.4993	1.4775	118.6044	118.8129
85	1.4304	1.4984	1.4676	118.5647	118.8437
86	1.4633	1.4774	1.4665	118.8119	118.0175
87	1.4506	1.4784	1.4634	118.7114	118.4384
88	1.4614	1.4782	1.4794	120.1809	118.4831
89	1.4445	1.4767	1.4733	119.7562	118.8981
90	1.4575	1.4896	1.4682	119.4919	118.5415

2.2. Results of comparing magnetic behavior of some molecules based on the frequency of aryl azo linkages in cyclopentadienides

The analysis of the numerous of aryl azo linkages on different positions of cyclopentadienides shows that the frequency of aryl azo linkages were increased in NICS (0) and decreased possibility of resonance consequent of aromatic effect (Figure 3).

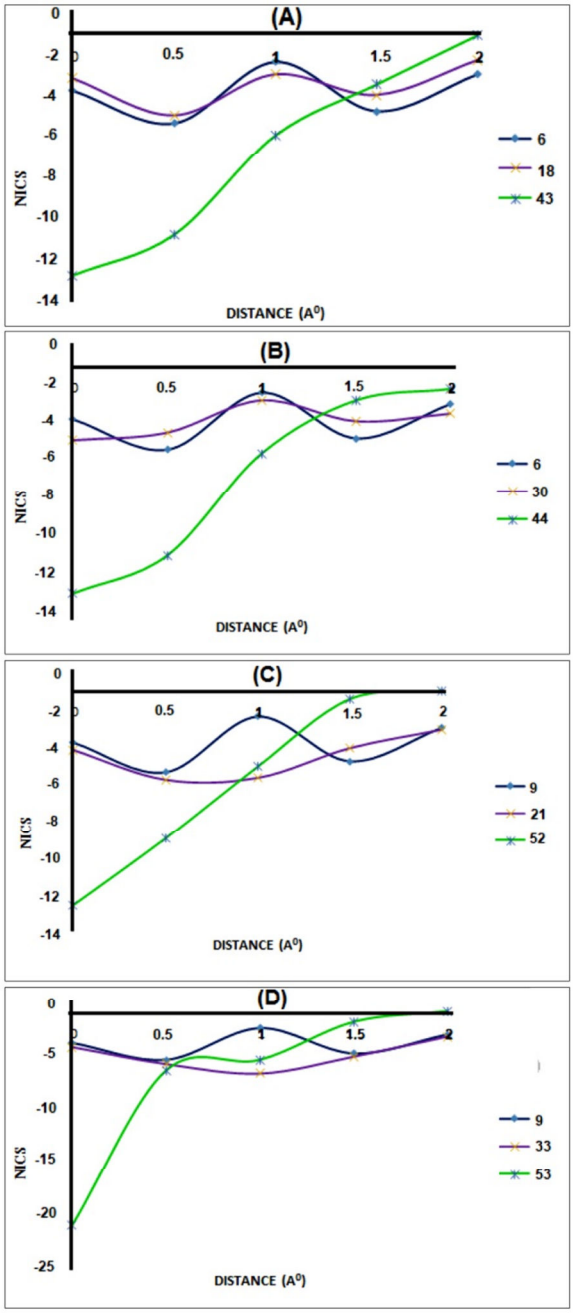


Figure 3: Comparing magnetic behavior of some molecules based on the frequency of aryl azo linkages in cyclopentadienides.

2.3. Results of comparing magnetic behavior of some molecules based on the type of phenyl's substitution in cyclopentadienides

First, the effect of type of substitutions which are resonating electron donors with nature of electron withdrawing field was analyzed in all of positions of cyclopentadienide compounds. The results indicate that aryl azo substitutions with different groups have close values of NICS at positions 2 and 3 of cyclopentadienide ring (Figure 4).

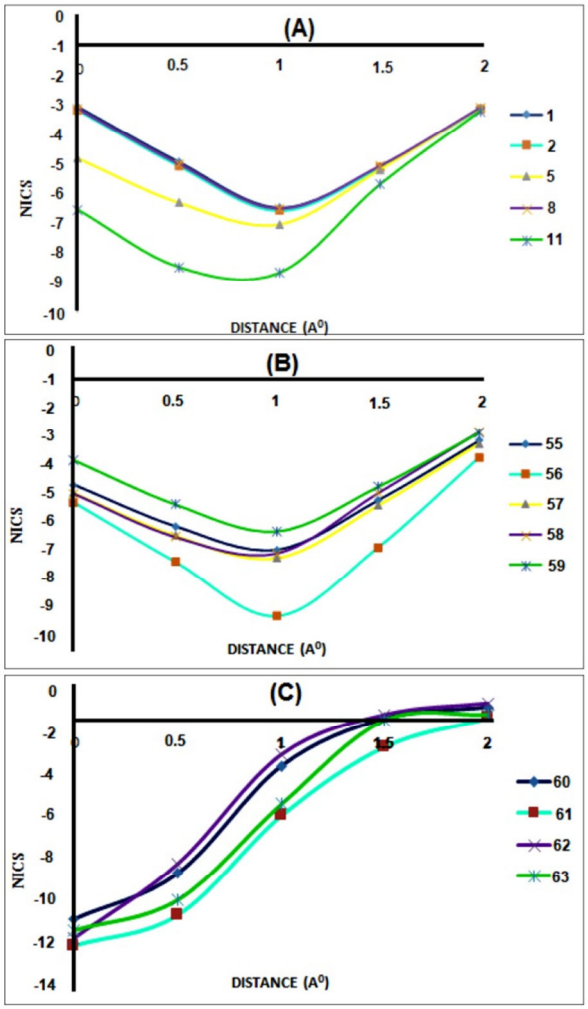


Figure 4: Comparing magnetic behavior of some molecules based on the type of phenyl's substitution in cyclopentadienides.

2.4. Results of comparing magnetic behavior of some molecules based on the position of phenyl's substitution in cyclopentadienides

The analysis of the position of same substitution such as nitro (which is a strong resonant and inductive electron withdrawing group) at various positions of phenyl azo linkages indicates that changing the position of nitro group (*ortho-, meta-* or *para-*), NICS values show lower change. The study on same effect of methoxy group was shown similar results (Figure 5).

2.5. Results of comparing magnetic behavior of some compounds in terms of the type of bridge

The analysis of some types of 1-bridges (azo, imine and vinyl) cyclopentadienide (Table 2) with electron withdrawing or electron donor substitutions indicated that the type of the studied bridges does not have significant effect on NICS values and the trends due to these bridges are almost the same (Figure 6).

The analysis of type of bridges 4-nitrophenylaznyl-linked cyclopentadienide 6 versus vinyl or imine-type bridges revealed that positive NICS (1) values. The results showed NICS (1) values of azo-type linkage is worse (Figure 6-diagram A). In general, the NICS values related to compounds with azo bridge are similar to vinyl-bridge (Figure 6) and the imine-type bridges that were synthesized from cyclopenta-2,4-dienecarbaldehyde and anilines consisted of electron withdrawing or electron donor substitutions showed better NICS index (Figure 7).

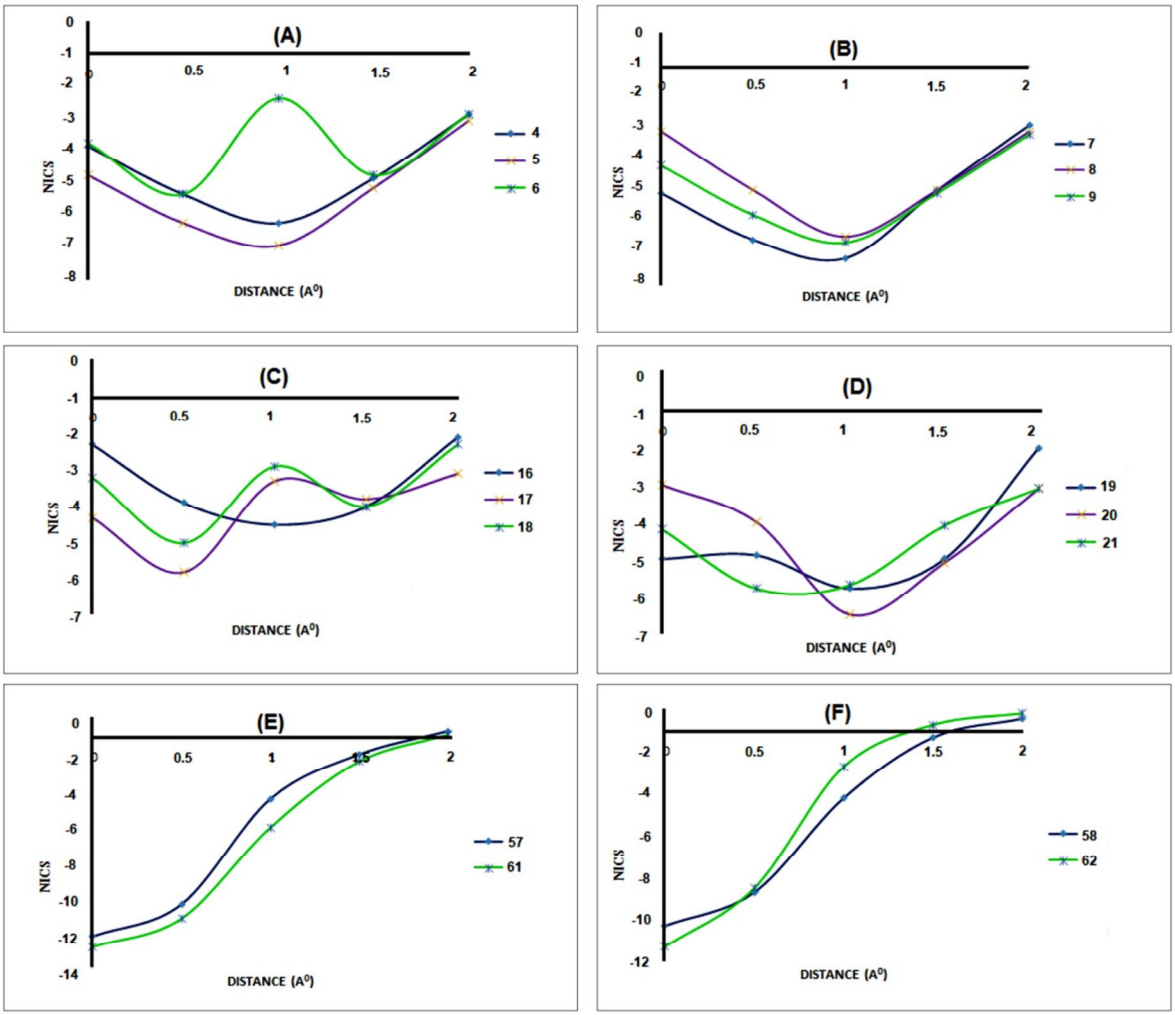


Figure 5: Comparing magnetic behavior of some molecules based on the position of phenyl's substitution in cyclopentadienides.

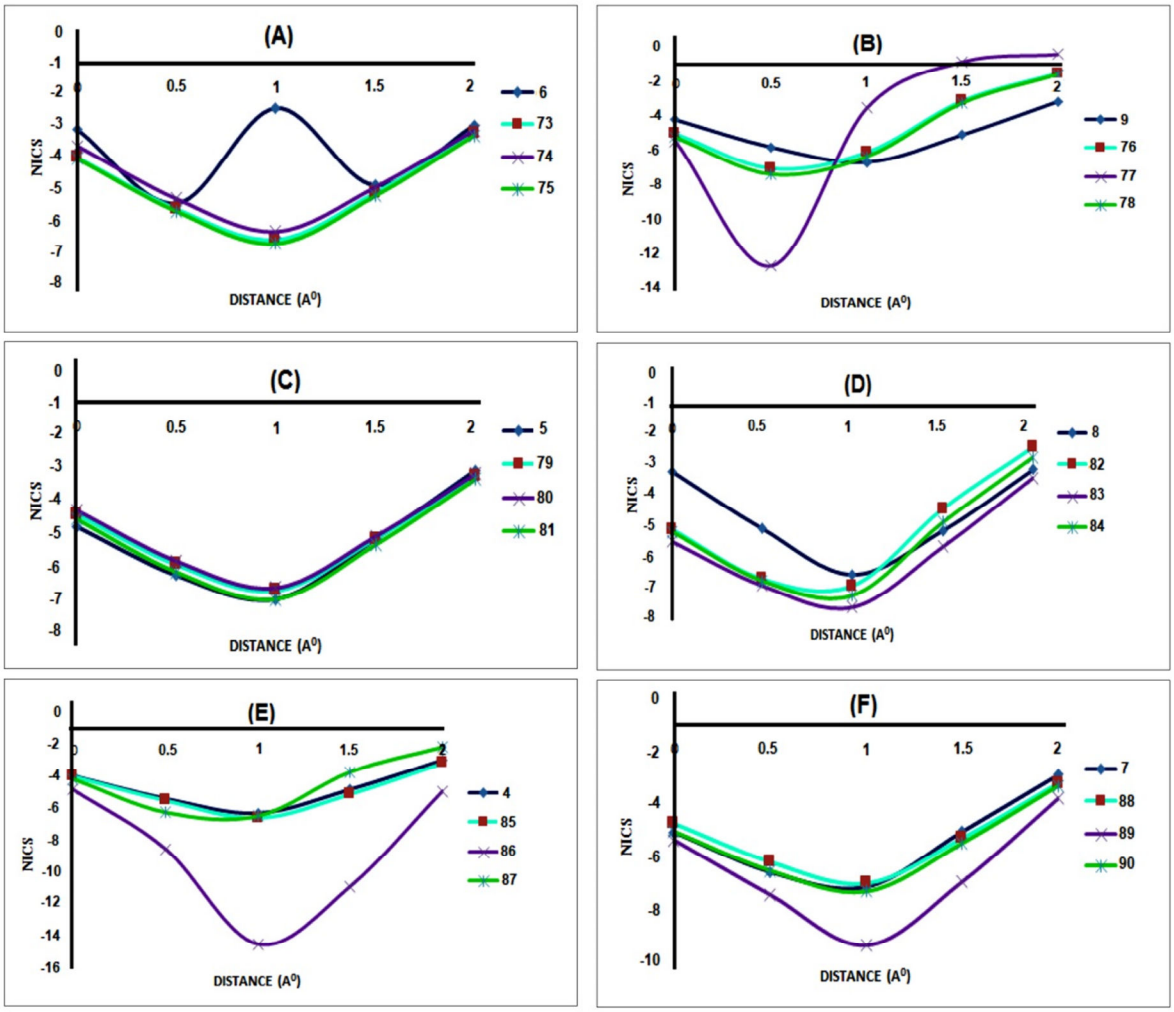


Figure 6: Comparing magnetic behavior of some compounds in terms of the type of bridge.

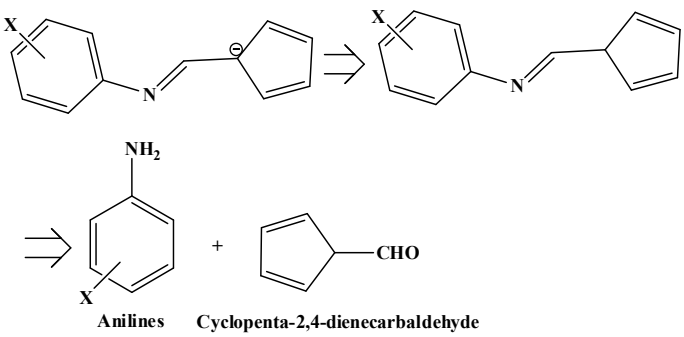


Figure 7: Imine-type bridges that were synthesized from cyclopenta-2,4-dienecarbaldehyde and anilines.

3. Conclusions

The analysis of data related to bond length and bond angle indicated that the length of bonds C_1-C_2 and C_3-C_4 is shorter of C-C single bond and it is between the length of C-C single bond (1.54 Å) and C=C double bond (1.34 Å). On the other hand, C_2-C_1-C_5 bond angle inclines from sp^3 hybridization to sp^2 hybridization. Therefore, regarding the analysis of bond length and bond angle, cyclopentadienide has aromatic properties. NICS values were measured at intervals of 0-2 Å for studied

compounds. The results of calculations show that NICS values consequent of aryl azo substitution at positions 1, 2 and 3 of cyclopentadienides is similar. Generally, increasing the number of azo-linked groups at various positions in cyclopentadienides is good and improves the aromatization by expanding the resonance systems. NICS (0) values showed the most improvement.

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