Cyclophanes. 16. Synthesis and Conformational Behavior of 2,11-Dithia[3.3](3,5)isoxazoloparacyclophane, 2,11-Dithia[3.3](3,5)isoxazolometacyclophane, and [2.2](3,5)Isoxazoloparacyclophane

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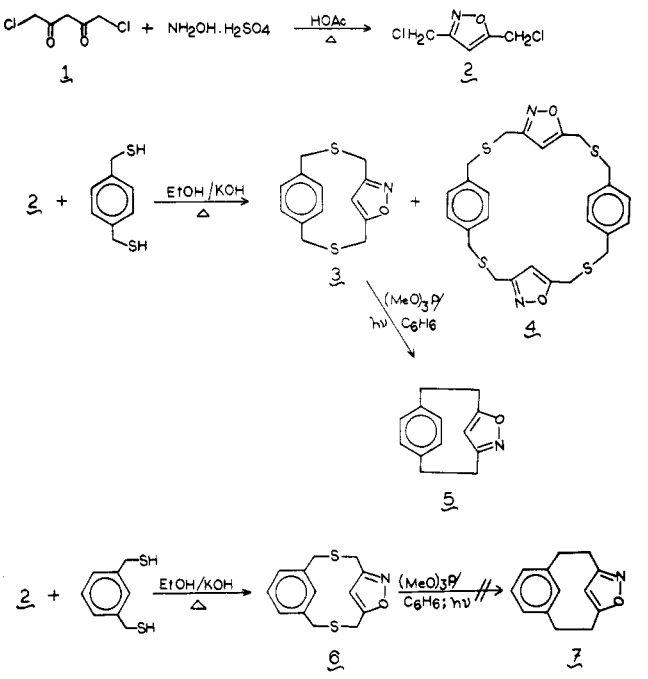
The synthesis of 2,11-dithia[3.3](3,5)isoxazoloparacyclophane (**3**), 2,11-dithia[3.3](3,5)isoxazolometacyclophane (**6**) and [2.2](3,5)isoxazoloparacyclophane (**5**) is described. Dithiaphanes **3** and **6** are prepared in 52.5% and 48.7% yields, respectively, by condensing 3,5-bis(chloromethyl)isoxazole with *p*-xylenedithiol and *m*-xylenedithiol. In the former reaction a tetramer, 2,10,19,27-tetrathia[2](3,5)isoxazolo[2]paracyclo[2](3,5)isoxazolo[2]paracyclophane (**4**) is also isolated (2.8% as two positional isomers). Sulfur extrusion from **3**, by photolysis, gives a 7% yield of [2.2](3,5)isoxazoloparacyclophane (**5**). Attempted extrusion of sulfur from **6** by photolysis was unsuccessful. No charge-transfer interactions seem to exist in **5** under neutral or acidic conditions. While both the aromatic rings and the aliphatic bridges are conformationally rigid on the NMR time scale in **5**, they are mobile in **3**. The coalescence temperature (T_c) for ring inversion in **3** occurs at −55 °C, and the $\Delta G^{\ddagger}$ for this process is 10.9 kcal/mol. The bridge flipping in **3** remains rapid even at −90 °C. In compound **6** the aromatic rings seem to be frozen in a syn orientation at temperatures up to 150 °C. Conformational inversion of the thia bridges, however, occurs freely above 90 °C and is restricted below −40 °C. Unfortunately, T_c and $\Delta G^{\ddagger}$ for this latter process could not be determined due to the complicated variable-temperature NMR spectra.

Over the past decade dynamic NMR studies have been carried out for a variety of cyclophanes in order to determine the conformational behavior in these systems as well as the associated stereochemical and energy requirements necessary for these processes.[2] Prior to our recent report on the synthesis and conformational properties of [2.2](2,5)oxazolo- and thiazolophanes,[3] no [2.2]heterophanes containing more than one heteroatom in the five-membered aromatic moiety had been documented.[4] In addition to our desire to study the conformational properties of heterophanes,[2d] our interest in incorporating five-membered heteroaromatics with two heteroatoms (such as oxazole, thiazole, imidazole, etc.) into the cyclophane framework stems from the fact that these nuclei constitute important structural units of several biologically significant molecules.[5] Furthermore, our continued interest in defining how charge-transfer interactions in cyclophanes are affected by placing fully developed charges into these macrocycles[6] suggested the use of these heteroaromatic units since in many instances they form charged slats by alkylation, especially when nitrogen is one of the heteroatoms. In this paper we describe the synthesis and dynamic behavior of 2,11-dithia[3.3](3,5)isoxazoloparacyclophane (**3**), [2.2](3,5)isoxazoloparacyclophane (**5**), and 2-11-dithia[3.3](3,5)isoxazolometacyclophane (**6**).[7]

Scheme I



Synthesis

The synthesis of **3**, **5**, and **6** are shown in Scheme I.[8] The preparation of the key precursor 3,5-bis(chloromethyl)isoxazole (**2**) was realized in over 80% yield by condensing dione **1**[9] with $NH_2OH{\cdot}H_2SO_4$ in refluxing acetic acid. Coupling of **2** with *p*-xylenedithiol was performed under high dilution and provided two compounds after chromatography in 52.5% and 2.7% yields. The major product (mp 161–162 °C; *m/e* 263) was characterized as disulfide **3** on the basis of spectral and microanalytical

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(7) [3,5](9)Isoxazolophane has been reported. Bradamante, S.; Fusco, R.; Marchesini, A.; Pagani, G. *Tetrahedron Lett.* **1970**, 11.

(8) This methodology is based on the procedure developed independently by Boekelheide and Jenny. (a) Boekelheide, V.; Reingold, I. P.; Tuttle, M. *J. Chem. Soc., Chem. Commun.* **1973**, 406. (b) Bruhin, J.; Jenny, W. *Tetrahedron Lett.* **1973**, 1215.

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0022-3263/83/1948-1341$01.50/0

methods. The minor product (mp 207–213 °C) exhibited an m/e 526 (m^+) and its ^1H NMR spectrum exhibited a sharp singlet at δ 7.06 (benzenoid protons) and two overlapping singlets (δ 5.75) for the isoxazole proton. The bridge S–CH_2 protons appeared as a multiplet between δ 3.55 and 3.86. Mass spectral fragmentation together with the chemical shifts of the aromatic protons[10] suggested a tetrameric structure for this compound, and it is assigned structure **4**.[11] We might point out that **4** represents a new macrocyclic system, and due to the presence of eight heteroatoms in the periphery of the structure, it might exhibit some potential for complexation. Interestingly, the isoxazole ring, a latent 1,3-dicarbonyl unit, has recently been incorporated into a macrocyclic structure for this purpose.[12]

Irradiation of a dilute solution of **3** in $(MeO)_3P$/benzene (3:1) with a medium-pressure Hanovia lamp (using a Vycor filter) provided **5**, after workup and extensive purification, in 7% yield. The low yield is perhaps due to the competing photofragmentation and rearrangement processes of the isoxazole ring which accompanies the photoextrusion process.[13] The ^1H NMR spectrum of compound **5** exhibited a complex multiplet between δ 2.5 and 3.23 which was assigned to the bridge CH_2 protons. The benzenoid protons were observed as two narrow multiplets at δ 6.65 and 7.0, and the isoxazole proton, as expected, appeared considerably shielded at δ 4.55 (singlet).

The ultraviolet spectrum of isoxazolophane **5**, which lacked fine structure as expected for a cyclophane,[14] exhibited a strong maximum at 230 nm (ϵ 6800) and a weaker one at 292.5 nm (ϵ 965). These two absorptions are probably due to the 3,5-disubstituted isoxazole moiety and the 1,4-disubstituted benzene moiety within **5**. Both absorptions are bathochromically shifted relative to 3,5-dimethylisoxazole (215 nm)[15] and *p*-xylene (274.5 nm),[16] and the shifts can be attributed to the distortions in the aromatic rings in **5** as has earlier been described for [2.2]paracyclophane.[14] No significant changes in the position of the absorption bands were observed when either cyclohexane or acetonitrile was used as the solvent, though a hypochromic effect on the 292.5-nm band was observed. Almost certainly this long wavelength band is not associated with charge transfer. In addition, the spectrum (in EtOH) remained practically unchanged when trifluoroacetic acid was added in dilute or high concentrations. Either protonation of the isoxazole moiety in **5** did not take place[17] or no significant charge transfer exists between the benzenoid and isoxazolium units if protonation did take place.

The attempted synthesis of **7** also utilized dichloride **2** which was coupled with *m*-xylenedithiol to furnish disulfide **6** (49%; mp 147–149 °C). The ^1H NMR spectrum revealed a broadened singlet at δ 6.56 (internal proton on the benzene ring) whereas the proton on the isoxazole ring appeared as a sharp singlet at δ 6.08. The remaining benzenoid protons appeared as a multiplet between δ 6.86 and 7.30. Since the internal protons (both on the benzene and the isoxazole ring) appear at a rather normal position in comparison with open-chain analogues,[10] it appears that **6** exists (at least in solution) in the syn conformation.[18] In the anti conformation these protons should experience a considerable upfield shift due to the ring anisotropy as is evident in other related systems.[19] To date we have not been successful in finding suitable conditions for effecting the photoextrusion of sulfur from **6**. Compound **6** was perhaps formed but does not survive the photolysis conditions due to the photolability of the isoxazole ring.

Conformational Behavior of Isoxazolophanes 3, 5, and 6

For the determination of the conformational properties of **3**, **5**, and **6** these compounds were studied by using variable-temperature NMR spectroscopy. ^1H NMR spectra of **3** were recorded from room temperature (23 °C) down to −85 °C. At 23 °C sharp singlets are observed for the benzenoid protons (δ 6.97) and the four different thia-bridged methylene protons (δ 3.26, 3.40, 3.42, 3.46). It is thus apparent that at ambient temperature both the rings and the thia bridges are undergoing rapid inversion relative to the NMR time scale. Coalescence was, however, observed at about −55 °C, and at −73 °C the absorption due to the benzenoid protons split into an AB quartet (δ 6.71, 10 Hz) and a broad singlet (δ 7.16). This data suggests that the isoxazole-ring flipping process has been retarded. (The thia-bridge inversion seemed to slow down at these temperatures as was indicated by the broadening of the signals associated with the bridge protons. The absorptions did not fully coalesce, however, even at −85 °C.) From the coalescence temperature (−55 °C) and the separation of the benzenoid proton signals at −73 °C, the rate of inversion (K') was calculated to be 46.5 s^{-1} with an associated Arrhenius energy of activation (ΔG^*) of 10.9 kcal/mol.[20] Dithia[3.3]metaparacyclophane (**8**) was reported to show no coalescence down to −90 °C;[19] thus the increased barrier to inversion in **3** is probably due to the smaller meta-bridged isoxazole ring.

In contrast to **3**, the ^1H NMR spectrum of **6** at room temperature exhibited overlapping multiplets (δ 3.53–3.90) for the thiahbridge methylene protons, suggesting that the bridges in this compound were undergoing inversion, albeit at a slower rate than was observed for **3**. As the temperature was raised, the multiplet began to collapse and ultimately gave rise to four sharp singlets (δ 3.86, 3.80, 3.70, and 3.69) at 95 °C. However, of these four singlets, the two central ones appeared earlier (i.e., at lower temperature, 50–55 °C) than the two outer ones (75–80 °C). This observation could be indicative of the unequal rates at which the two bridges undergo the inversion process.[21] As the temperature was lowered from ambient, the multiplicity of the absorption due to these methylene-bridge protons increases with concomitant sharpening of the signals. At about −45 °C, 12 lines could be observed out of the 16 lines expected due to the geminal coupling (AB)

(10) In 3,5-dimethylisoxazole the ring proton appears at δ 5.80. See: "Sadtler Standard NMR Spectra"; Vol. 8.

(11) Two possible positional isomers can result by two different modes of coupling. Though a single spot was observed on TLC in various solvents, the broad melting point and ^1H NMR spectrum (two overlapping singlets for the isoxazole ring protons) clearly indicate a mixture of two isomers. Only one, however, is shown in Scheme I.

(12) Auricchio, S.; Ricca, A.; Vajnadepava, O. *J. Hetrocycl. Chem.* **1981**, 1471.

(13) (a) Sata, T.; Saita, K. *J. Chem. Soc., Chem. Commun.* **1974**, 781. (b) Sata, T.; Yamamoto, K.; Fukui, K. *Chem. Lett.* **1973**, 11.

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(15) Wiley, R. H. In "Heterocyclic Compounds"; Weissberger, A., Ed.; Interscience: New York, 1962; p 177.

(16) "Sadtler Standard Ultraviolet Spectra"; Vol. 2.

(17) Isoxazoles in general are very weak bases. See: Speroni, G.; Pino, P. *Gazz. Chim. Ital.* **1950**, *80*, 549.

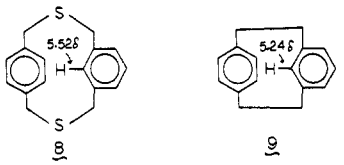
(18) 2,11-Dithia[3.3]metacyclophane has been shown to exist in the solid phase as well as in solution in the syn conformation. The internal proton appears relatively unshielded. See: Anker, W.; Bushnell, W. G.; Mitchell, R. H. *Can. J. Chem.* **1979**, *57*, 3080.

(19) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.

(20) Calculations were based on the following equations: $K = \pi\Delta\nu/2^{1/2}$; $\Delta G^* = 2.303RT_c(10.319 - \log K + \log T_c)$. See: Akabori, S.; Hayashi, S.; Nawa, M.; Shiomi, K. *Tetrahedron Lett.* **1969**, 3737.

(21) This is quite conceivable in view of the nonidentical nature of the two thia bridges.

of four different bridging methylene groups. At this temperature the bridge-flipping process seems to have stopped. However, because of the complexity of the multiplet we could not determine coalescence temperatures or chemical shift separations with reasonable accuracy.[22] During the above variable-temperature changes involving the bridge protons no appreciable changes were noticed in the absorption of the aromatic protons of **6** from +150 to −50 °C. This behavior is analogous to that of dithia[3.3]metacyclophane and suggests the absence of ring-inversion processes.[18] Isoxazolophane **5** appears to adopt a parallel (or quasi-parallel) orientation of the rings as deduced by the presence of two narrow multiplets at δ 6.65 and 7.0 for the ortho-coupled protons on the benzenoid ring, and thus, at room temperature the molecule exists in a conformationally frozen state. Variable-temperature ^{1}H NMR spectra scanned up to 150 °C remained essentially unchanged. On the basis of a minimum coalescence temperature of 150 °C and the existing separation of 31.5 Hz between the benzenoid absorptions, a minimum energy of activation (ΔG^*) can be calculated to be 21 kcal/mol. In contrast, [2.2]metaparacyclophane (**9**) has been reported to undergo ring inversion at elevated temperature with an energy of activation of about 20 kcal/mol.[2d,23]



8 **9**

The activation energy for these conformational processes reflects the degree of steric repulsion (i.e., the intergroup distance) between the internal hydrogen (or any other group) and the opposite ring in the transition state.[2e] We believe that the higher activation energy for the ring inversion in **5** relative to **9** could be attributed, at least in part, to a more severe destabilizing interaction between the isoxazole proton and the proximate ring. Available evidence seems to support this contention. For instance, the shielding increment for the internal proton in going from **8** (δ 5.52) to **9** (δ 5.24) is δ 0.28,[19,24] whereas the corresponding shift difference between **3** and **5** is as much as δ 0.46. Since the shielding effects are a function of the distance between the interacting groups in question, the isoxazole ring proton in **5** ought to be situated closer to the proximate bezenoid ring than would the internal hydrogen of the meta-bridged ring in **9**. Recent studies by Itô et al. on several paracycloazulenophanes such as [2.2](1,3)azulenoparacyclophane and [2.2](5,7)azulenoparacyclophane have clearly shown that the activation energy for the ring interconversion increases on going from the seven- to the five-membered ring.[25] Our results in the isoxazole systems agree with Itô's observations.

The ring-flipping process has important stereochemical implications for cyclophanes **3**, **5**, and **6**. The presence of the unsymmetrical heteronucleus (isoxazole) in the phane introduces an element of dissymmetry to the molecule. Thus, isoxazolophane **5**, due to its conformational rigidity, exists as a racemic mixture and is potentially resolvable. However, because of relatively free interconversions, disulfides **3** and **6** exist as mixtures of rapidly interconverting stereoisomers. Attempts to alkylate the nitrogen atom of the isoxazole ring in **5** with methyl iodide or Meerwein's salt (in order to determine whether salts could be prepared for resolution) have not been successful.[26]

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ultraviolet and visible spectra were recorded on a Perkin-Elmer Model 683 grating spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units with tetramethylsilane as an internal standard. Variable-temperature spectra were recorded on a Perkin-Elmer Model R-32 and a Bruker Model WH-90 spectrometer with Me_2SOd_6 and CD_3NO_2 as solvents for high temperatures and hexamethyldisiloxane as an internal standard. Low-temperature spectra were recorded in CD_2Cl_2 and $(CD_3)_2CO$ as solvents with tetramethylsilane as an internal standard. Microanalyses were performed by Galtraith Laboratories, Knoxville, TN.

3,5-Bis(chloromethyl)isoxazole (2). 1,5-Dichloropentane-2,4-dione[9] (2.6 g, 15.3 g mmol), hydroxylamine sulfate (2.1 g, 12.8 mmol) and glacial acetic acid (15 mL) were stirred at room temperature for 30 min and then gently refluxed for 4 h under N_2. The reaction mixture was then cooled to room temperature and poured onto a mixture of crushed ice and ether. The solution was neutralized by using a saturated solution of $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with ether, and the total extract was washed once with brine and dried over Na_2SO_4. After solvent evaporation the crude oil was chromatographed (silica gel, $CHCl_3$) to give **2** (2.25 g, 88% yield) as a pale yellow oil: IR (neat) 3135, 3010, 2940, 1600, 1440, 1265, 1160, 1125, 1005, 940, 880 cm^{-1}; NMR ($CDCl_3$) δ 4.58 (2 H, s), 4.60 (2 H, s), 6.40 (1 H, s); MS, *m/e* 166 (M^+).

2,11-Dithia[3.3](3,5)isoxazoloparacyclophane (3). To a refluxing solution of ethanol (1 L) containing KOH (2.1 g, 37.5 mmol) was added, over a period of 12 h, a solution of **2** (2.5 g, 17.47 mmol) and *p*-xylenedithiol (3.0 g, 17.64 mmol) in benzene (250 mL) under N_2. After being refluxed for an additional 4 h, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated and gave a crude solid. This material was chromatographed (silica gel, $CHCl_3$) to give **3**: 2.4 g (52.5%); mp 161–162 °C (from C_2H_5OH/CH_2Cl_2); IR (KBr) 3115, 2940, 2900, 1582, 1510, 1450, 1420, 1260, 995, 840 cm^{-1}; NMR ($CDCl_3$) δ 3.26 (s, 2 H), 3.40 (s, 2 H), 3.42 (s, 2 H), 3.46 (s, 2 H), 5.0 (s, 1 H), 6.97 (s, 4 H); MS, *m/e* 263 (M^+), 104, 91. Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.31; H, 4.94; N, 5.32; S, 24.33. Found: C, 59.52; H, 5.11; N, 5.21; S, 24.79.

Further elution with $CHCl_3$ gave tetramer **4** (125 mg, 2.75%) as a mixture of two positional isomers: mp 207–213 °C; IR (KBr) 3115, 1602, 1505, 1432, 1422, 1410, 1232, 1130, 1005, 825, 773 cm^{-1}; NMR (Me_2SO–d_6) δ 3.55–3.86 (m), 5.75 (2 overlapping s), and 7.06 (s) in the ratio of 8:4:1; MS, *m/e* 526 (M^+), 263, 231, 135, 104, 91.

[2.2](3,5)Isoxazoloparacyclophane (5). Dithiaphane **3** (1.0 g, 3.8 mmol) was dissolved in $(MeO)_3P$ (225 mL) and thiophene-free benzene (75 mL) and irradiated under N_2 with a medium-pressure Hanovia lamp (450 W) with a Vycor filter. The progress was monitored every 4 h by hydrolysis of an aliquot with H_2O, extracting with benzene, drying, concentrating and taking an NMR spectrum of the residue. Product formation did not reflect the corresponding drop in the starting material concentration. This appears to be due to decomposition which accompanies the photoextrusion. After 36 h of irradiation, integration of relevant peaks in the NMR spectrum indicated the presence of about 10% of the product, 3% starting material, and unidentified products. At this time the reaction mixture was hydrolyzed with H_2O (2 h) and extracted thoroughly with benzene containing 10% ethyl acetate. The organic layer was washed several times with H_2O, dried, and concentrated to give a crude oil. Initial purification was done by preparative TLC (silica gel; hexane/ethyl acetate, 3:1). Removal of the least polar spot (R_f

(22) Currently we are synthesizing the tetradeuterated analogue of **6** (D in the benzylic positions) to precisely study and calculate the kinetic parameters of these separate bridge-flipping processes.
(23) Vogtle, F. *Chem. Ber.* **1969**, *102*, 3077.
(24) Boekelheide, V.; Anderson, P. H.; Hylton, T. A. *J. Am. Chem. Soc.* **1974**, *96*, 1558.
(25) Itô, S. *Pure Appl. Chem.* **1982**, *54*, 957.
(26) Davis, M.; Deady, L. W.; Homfeld, E. *Aust. J. Chem.* **1974**, *27*, 1221.

0.25–0.37) afforded a material which was found to consist of approximately 65% of **5**, 25% of **3**, and a remaining unidentified product by NMR spectroscopy. The starting material could be selectively removed by crystallization from 2-propanol. The filtrate, after concentration and two crystallizations (ethyl acetate/hexane) gave **5**: 61 mg (7%); mp 155–157 °C; IR (KBr) 2915, 1582, 1445, 1405, 1325, 1195, 1090, 995, 880, 865, 805 cm^{-1}; NMR ($CDCl_3$) δ 2.5–3.23 (m, 8 H), 4.55 (s, 1 H), 6.65 (m, 2 H), 7.0 (m, 2 H); MS, *m/e* 199 (M^+), 104, 92, 79. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 7.03. Found: C, 78.60; H, 6.71; N, 7.01.

2,11-Dithia[3.3](3,5)isoxazolometacyclophane (6). A solution of **2** (2.25 g, 13.55 mmol) and *m*-xylenedithiol (2.25 g, 13.23 mmol) in benzene (200 mL) was added, over a period of 14 h and under N_2, to a refluxing solution of ethanol (1 L) containing KOH (1.5 g). After being stirred for an additional 4 h, the reaction mixture was filtered through Celite, and the filtrate was concentrated to give a crude solid. This was chromatographed (silica gel, $CHCl_3$) and furnished **6**: 1.736 g (48.7%); mp 147–149 °C (C_2H_5OH/CH_2Cl_2); IR (KBr) 3115, 2930, 1605, 1426, 1400, 1280, 1218, 1135, 1003, 932, 843, 795 cm^{-1}; NMR ($CDCl_3$) δ 3.53–3.9 (m, 8 H), 6.08 (s, 1 H), 6.56 (br s, 1 H), 6.86–7.30 (m, 3 H); MS, *m/e* 263 (M^+), 109, 91. Anal. Calcd for $C_{13}H_{13}NOS_2$: C, 59.31; H, 4.94; N, 5.32; S, 24.33. Found: C, 59.47; H, 4.99; N, 5.28; S, 24.63.

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Registry No. **1**, 40630-12-4; **2**, 84987-94-0; **3**, 84987-95-1; **4**, 84987-96-2; **5**, 84987-97-3; **6**, 84987-98-4; **7**, 84987-99-5; *p*-xylenedithiol, 105-09-9; *m*-xylenedithiol, 41563-69-3; $NH_2OH·H_2SO_4$, 10046-00-1; $(MeO)_3P$, 121-45-9.

A Bond Order Approach to Ring Current and Aromaticity

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An alternative approach to ring current and aromaticity is developed related to bond order. The concept is general enough to include nonplanar and nonbenzenoid rings as well as ions. Calculations are performed with the semiempirical MO method SINDO1 on a representative large number of mono- and polycyclic ring systems up to four rings. Also some excited states are investigated. Most conclusions about aromaticity are in agreement with those reached by a topological index based on resonance energies. Exceptions to this agreement are also presented and explained.

The concept of aromaticity can be found in any textbook of theoretical organic chemistry.[1,2] A conjugated ring system is usually called aromatic if its stability is considerably increased compared to that of its classical localized structure. In the elementary discussion, much attention is given to the Hückel rule that a ring system with $4n + 2$ electrons is aromatic, whereas a system with $4n$ electrons is not. Aromatic systems in this sense are benzene, pyridine, pyrrole, furan, cyclopentadienyl anion, etc. However, more sophisticated arguments have to be given when it comes to the point of comparing the degree of aromaticity. Difficulties with the Hückel rule arise with the aromaticity of larger annulenes. Dewar[2] emphasizes that resonance energies calculated by the Hückel method cannot be used as indices for classification of aromaticity. He advances the idea of resonance energies in an SCF framework referring to standard bond energies of ficticious single and double bonds in rings. His result is that from the *n*-annulenes, the compounds with $n = 6$ and 10 are aromatic, those with $n = 4$ and 8 are antiaromatic, and the rest are slightly aromatic or nonaromatic. The situation was comprehensively reviewed by Bergmann and Agranat[3] in 1970. From the ten criteria for aromaticity summarized in their article we shall concentrate only on the following important ones: (1) Lack of reactivity with respect to addition reactions, (2) very low enthalpy of the ground state, (3) sustained induced ring current.

In particular, we shall show that lack of bond alternation is not a necessary nor sufficient criterion for aromaticity. More recently a graph-theoretical approach to aromaticity has been advanced. Trinajstić and co-workers[4] have defined a topological resonance energy and applied this method successfully to hydrocarbons. Aihara[5] extended the graph-theoretical approach to unusual ions. His recent work[6] is addressed to the question of whether oxocarbon dianions are really aromatic. In the following section we develop an alternative approach to aromaticity based on the ring current concept. We relate ring current and bond order. We present an application of this concept to more than 70 ring systems. These include monocyclic and polycyclic rings, exotic systems, and excited states. We suggest that the graph-theoretical approach by Aihara can be misleading in crucial cases.

Method

Several years ago, we introduced a maximum bond order principle[7] which results in the definition of a bond order between any pair of atoms in a molecule, once an LCAO MO wave function is obtained by an ab initio or semiempirical MO method. We showed that the principle can be applied to CI wave functions[8] for which a density matrix in the LCAO framework can be defined. The bond order is the weighted sum of eigenvalues of the two-center parts of the density matrix of the pair of atoms considered.

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