Geometry-Optimized INDO Calculations on 1,3-Donor–2,4-Acceptor-Substituted Cyclobutadienes

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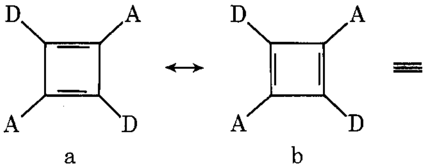
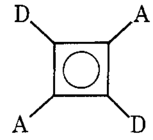
Geometry-optimized SCF–MO calculations, in the INDO approximation, were performed on a series of donor–acceptor substituted cyclobutadienes to include 1,3-diamino-2,4-dicyanocyclobutadiene (III), 1,3-dihydroxy-2,4-dicyanocyclobutadiene (IV), 1,3-difluoro-2,4-dicyanocyclobutadiene (V), 1,3-diaminocyclobutadiene (VI), 1,3-dicyanocyclobutadiene (VII), and 1,2-diamino-3,4-dicyanocyclobutadiene (VIII). The most stable geometry of III–VII was D_{2h} parallelograms and not the D_{2h} square or C_{2h} rectangular geometries. Electron-donating groups caused the ring angles at that point to be >90° while electron-withdrawing groups caused a decrease in the ring angle <90°. Using III and VIII as model systems, it was shown that 1,3-donor–2,4-acceptor cyclobutadienes are more stable than their 1,2-donor–3,4-acceptor analogs in the square, rectangular, and parallelogram geometries. These results are compared to previous calculations and experimental results.

Unlike highly unstable cyclobutadiene, donor–acceptor substituted cyclobutadienes are stable molecules whose chemistry has been established.[1-3] However, the structure of these derivatives is a topic of somewhat more controversy. The reported X-ray structure of diethyl 2,4-bis(diethylamino)cyclobutadiene-1,3-dicarboxylate (I where D = $-NEt_2$ and A = –COOEt) found all the ring carbon–carbon bond lengths to be equal,[4] in agreement with resonance hybrid Ic. Furthermore, the NCH_2 proton NMR signals were equivalent down to −46° in accordance with Ic.[5,6] On the other hand, the strongly nonvertical uv spectrum[5,6] spanning 8000 cm^{-1} (λ_{max} 25,500 cm^{-1}, ϵ_{max} 2.37) suggested that the ground and first excited state potential surfaces were markedly different. Also, the photoelectron spectrum of this molecule showed that the shape and binding energies of C_{1s}, N_{1s}, and O_{1s} were very similar to those of β-diethylaminoethyl acrylate. Further, the low-energy π bands of these molecules (7.55 and 7.63 eV, respectively) are only trivially different. These observations are incompatible with the D_{2h} (square) structure and were explaned on the basis of localized double bonds linked through single bonds.[5]

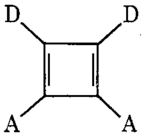


a b

I



c



II

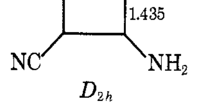
MINDO/2 calculations of Weiss and Murrell indicate that a low barrier exists for the interconversion of the energetically equivalent valence tautomers Ia and Ib.[7] These calculations on donor–acceptor molecules I and II (where D = $-NEt_2$ and A = –COOEt) showed that distortion of geometry toward double bond fixation (pseudo D_{2h} to C_{2h} symmetry) lowered the energy in both, but that the effect was appreciably larger in II than in I. Furthermore, these calculations predicted a 3 kcal/mol energy difference between D_{2h} (delocalized) and C_{2h} (localized) 1,3-diamino-2,4-dicyanocyclobutadiene. The MINDO/2 results differ from calculations of Hoffman,[8] who predicted I to be more stable than II based on a greater symmetry-favored splitting of the frontier orbital pair which is degenerate in square cyclobutadiene itself. Hoffman had assumed that the ring bond lengths remained the same (D_{2h}).[8]

In view of the results described above, we performed a series of SCF-MO calculations in the INDO[9,10] approximation on the five model systems: 1,3-diamino-2,4-dicyanocyclobutadiene (III), 1,3-dihydroxy-2,4-dicyanocyclobutadiene (IV), 1,3-difluoro-2,4-dicyanocyclobutadiene (V), 1,3-diaminocyclobutadiene (VI), and 1,3-dicyanocyclobutadiene (VII). The geometry of these compounds was optimized with respect to energy to establish the ground state structure. The use of optimized geometries stands in sharp contrast to that of previous studies.[7,8] In addition the stabilities of diaminodicyanocyclobutadienes of types I and II were compared.

Results

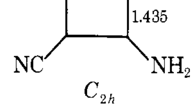
The CNINDO program QCPE no. 141 was employed, as described earlier,[11-18] with a model builder program. Both were modified for use on a Univac 110 computer. Figure 1 summarizes the optimized geometries and gives the charge densities for III–V. For donor–acceptor cyclobutadienes the following procedure was used. The relative energies of various geometries of III–VIII are summarized in Table I.

Starting with D_{2h} symmetry (optimized bond lengths were obtained for that symmetry, IIIa) the ring was modified to a rectangle, C_{2h}, by elongating one parallel pair of the ring CC bonds (see IIIb). Then the other parallel pair was shortened as shown in IIIc. Then the entire structure was optimized without restrictions. This resulted in a parallelogram geometry with D_{2h} symmetry. For IIIa–c all lengths used were optimized (except for the ring bonds in IIIb and IIIc). The substituents' axes bisected the ring an-



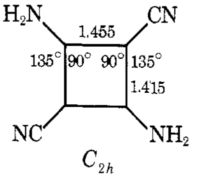
D_{2h}

IIIa



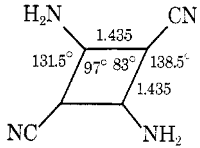
C_{2h}

IIIb



C_{2h}

IIIc



D_{2h}

IIId

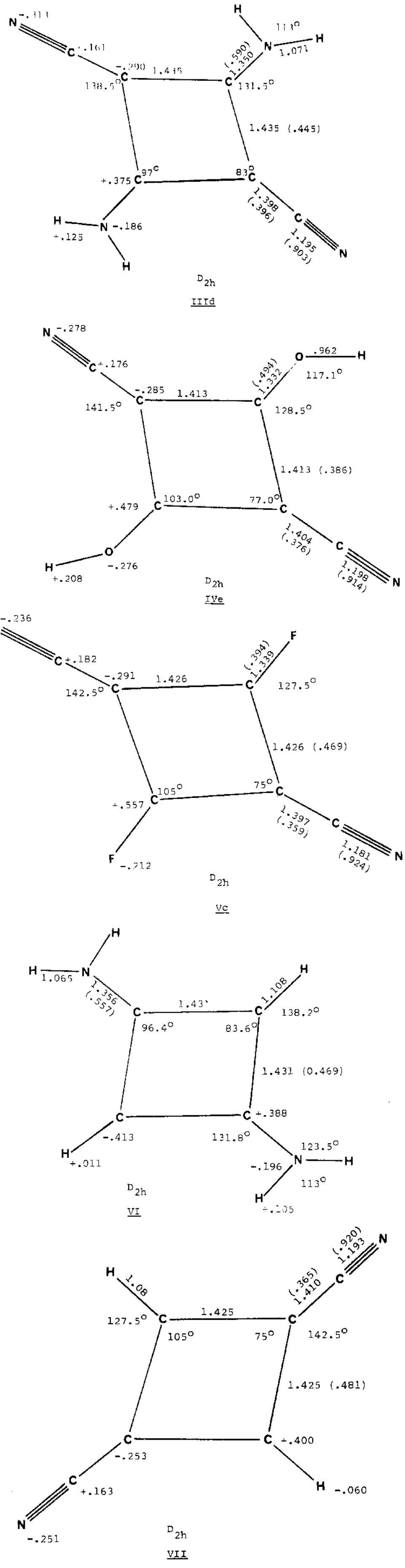


Figure 1. Optimized geometries, charge densities, and π-bond orders for donor and acceptor substituted cyclobutadienes III–VII. π-bond orders are given in parentheses.

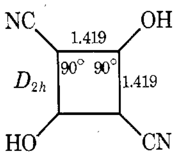
Table I
Relative Energies of Different Geometries of Donor-Acceptor Substituted Cyclobutadienes[a]

Structure	Symmetry	Shape	Relative energy,[b] kcal/mol
IIIa	D_{2h}	Square	7.8
IIIb	C_{2h}	Rectangle	8.0
IIIc	C_{2h}	Rectangle	8.1
IIId	D_{2h}	Parallelogram	0
IVa	D_{2h}	Square	12.7
IVb	C_{2h}	Rectangle	21.6
IVc	D_{2h}	Parallelogram	8.8
IVd	C_{2h}	Parallelogram	9.0
IVe	D_{2h}	Parallelogram	0
Va	D_{2h}	Square	29.5
Vb	C_{2h}	Rectangle	26.0
Vc	D_{2h}	Parallelogram	0
VI	D_{2h}	Square	3.6
VI	D_{2h}	Parallelogram	0
VII	D_{2h}	Square	20.6
VII	D_{2h}	Parallelogram	0
VIIIa	C_{2v}	Square	19.3
VIIIb	C_{2v}	Rectangle	0
VIIIc	C_s	Parallelogram	11.4
VIIId	C_{2v}	Trapezoid	82.3
VIIIe	C_{2v}	Trapezoid	58.7

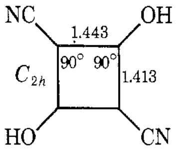
[a] Structures have each been geometry optimized with the exception of the bonds and angles being distorted to give the various geometries (see text for details). [b] The energies above 0 kcal mol^{-1} are less stable structures relative to the most stable structure (the one with a relative energy of zero). Comparison is only valid with other structures of the same molecule (i.e., IIIa with IIIb,c, or d but not IIIa with IVe, etc.)

gles. Optimizations all gave smooth paraboloid type potential wells. In the D_{2h} parallelogram geometry all the ring angles and lengths were optimized followed by complete optimization without restriction to IIId. Figure 1 summarizes the final optimized geometries and gives their total charge distributions and π-bond orders.

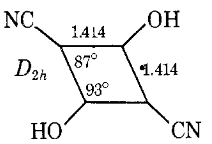
In contrast to the MINDO calculations of Weiss,[7] the optimized square geometry, IIIa, was 0.2 and 0.3 kcal/mol *more stable* than rectangular geometries IIIb and IIIc. More important, the square and rectangular geometries were significantly *less stable* than the parallelogram geometry IIId by 7.8, 8.0, and 8.1 kcal mol^{-1}, respectively. A similar analysis was performed on 1,3-dihydroxy-2,4-diaminocyclobutadiene (IV). The optimized square geometry IVa was more (8.9 kcal mol^{-1}) stable than the rectangular distortion IVb. Slight deformation of IVa to IVc parallelogram resulted in 3.9 kcal mol^{-1} increase in stability, but elongating one pair of sides (to IVd) caused only a tiny energy change (0.2 kcal mol^{-1}). However, deformation of the IVa to the completely optimized parallelogram geometry IVe



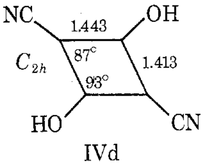
IVa



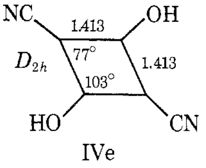
IVb



IVc



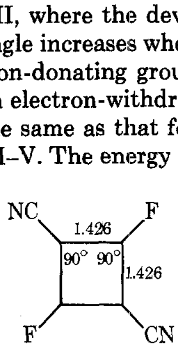
IVd



IVe

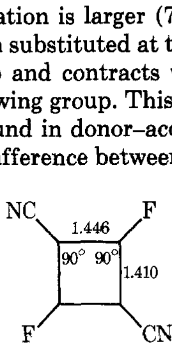
resulted in the most stable (12.7 kcal mol^{-1} more stable than IVa) structure.

1,3-diaminocyclobutadiene (VI), and 1,3-dicyanocyclobutadiene (VII), also were predicted to distort from the square D_{2h} to the parallelogram D_{2h} symmetry. Their optimized structures are given in Figure 1. In VI a small distortion of the ring angles (96.4 and 83.6°) occurs compared to VII, where the deviation is larger (75 and 105°). The ring angle increases when substituted at that point with an electron-donating group and contracts when substituted with an electron-withdrawing group. This trend in VI and VII is the same as that found in donor–acceptor cyclobutadienes III–V. The energy difference between square and parallelogram D_{2h} geometries in VI was 3.6 kcal mol^{-1}, while for VII a larger difference (20.6 kcal mol^{-1}) was found.



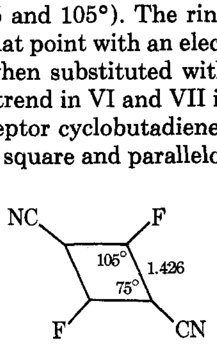
D_{2h}

Va



C_{2h}

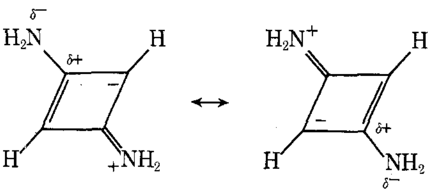
Vb



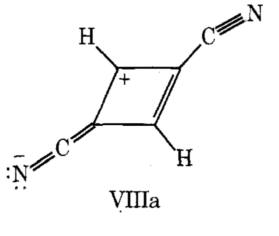
D_{2h}

Vc

The charge distribution in VI shows a significant buildup of negative charge at the unsubstituted carbons (−0.413), while the amino-substituted carbons are significantly positive (+0.388). The nitrogen atoms contain significant negative charge (−0.196) owing to strong σ polarization of the C–N bond toward N. However, examination of the π system confirms that the nitrogen p orbital (perpendicular to the molecular plane) is back donating electron density to the ring. The C–N π-bond order (0.557) is greater than the ring C–C π-bond orders (0.469). Thus, π-delocalization can be represented by hybrids VIa,b and VIIa below.



VIa VIb



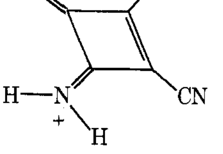
VIIIa

In contrast to VI, a significant positive charge density exists at the unsubstituted ring carbons in VII (+0.400) whereas the substituted ring carbons are negative (−0.253) to about the same extent as the cyano group nitrogens are (−0.250). Examining the σ and π systems carefully shows that an extensive depletion of the π-electron density from the unsubstituted carbon largely accounts for this. The π-bond orders follow: ring C–C, 0.481; the ring C–CN, 0.365; and the CN, 0.920.

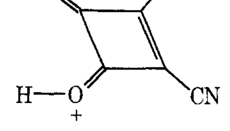
The equal-sided parallelogram geometry was also favored in V. Deforming Va to Vc resulted in a 29.5 kcal mol^{-1} lowering of the energy. Va was 3.55 kcal mol^{-1} less stable than Vb.

Thus a clear picture emerges within the framework of the INDO SCF–MO modification. Donor–acceptor cyclobutadienes of type I are most stable in the equal-sided parallelogram geometries shown in Figure 1. Furthermore, confining the ring angles to 90°, one sees that distortion from square (delocalized) to rectangular (localized) geometry results in a small destabilization. This is in conflict with the results of Weiss, but in his reported calculations geometry optimizations were not made.[7] Thus, it is not possible to be sure if MINDO favors the square, rectangular, or parallelogram structure, because it is necessary to optimize geometry to obtain the inherent results predicted by any calculational model.

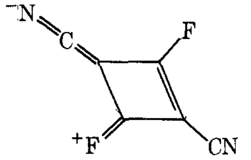
Charge Distributions in III–V. Significant contribution by resonance structures such as IIIe were not supported by the calculations. In III the amino nitrogen's charge (−0.186) and cyano nitrogen's charge (−0.313) were similar to the charges on the corresponding atoms of VI and VII (−0.196 and −0.250), suggesting only a modest contribution by IIIe. However, π donation to the ring by amino nitrogen (in III), hydroxy oxygen (in IV), and fluorine (in V) was occurring.[20] Also the cyano nitrogens were accepting π electrons from the ring. This was counteracted by polarization of the ring carbon σ bonds toward amino nitrogen, oxygen, and fluorine in III–V, respectively. In each case the ring, taken as a whole, was positively charged and the order of this effect was V > IV > III.



IIIe



IVf

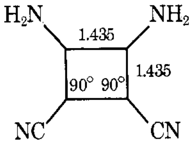


Vd

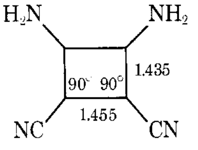
π-Bond Orders III–V. The π-bond orders also support the contention that resonance hybrids IIIe, IVf, and Vd do not significantly contribute. For example, in III the π-bond orders of H_2N–C (0.590) and C–CN (0.396) may be compared to those of VI (H_2N–C = 0.557) and VII (NC–C = 0.365). The slightly larger values in III, relative to VI and VII, argue for very small contributions by hybrid structure IIIe. A similar comparison of the C–CN π-bond orders in IV and V vs. that in VII suggests that IVf and Vd contribute only slightly. The π-bond orders are listed in Figure 1.

Relative Stability of Type I and Type II Donor–Acceptor Cyclobutadienes. Preliminary calculations were made on several geometries of 1,2-diamino-3,4-dicyanocyclobutadiene (VIII), as a model type II molecule. Complete optimization of all bond lengths and angles was not carried out and the total energy surfaces were not completely established. However, the lengths and angles employed were not far from the optimized structures, and further optimization would not be expected to change the trends established below. The C–NH_2, C–CN, C≡N, and N–H lengths employed were 1.350, 1.398, 1.195, and 1.072 Å, respectively, and an H–N–H angle of 113° was used.

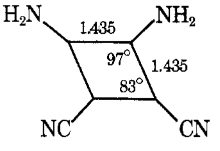
The rectangular, C_{2v}, geometry VIIIb was 19.3 kcal mol^{-1} more stable than the C_{2v} square, VIIIa. The C_s parallelogram, VIIIc, was 7.9 kcal mol^{-1} more stable than square VIIIa. Since in VI, VII, and the type I molecules, III–V, it was clear that the ring angles were >90° where a donor substituent was attached and <90° where an acceptor was attached, it was considered possible that VIII might favor a C_{2v} trapezoid geometry such as VIIId. Thus, VIIIa was deformed by slightly closing the ring angles at the position of the cyano substituents to give VIIId. However, this geometry was far less stable (by 63 kcal mol^{-1}) than VIIIa. Also, the trapezoid geometry VIIIe, where the angles at the cyano groups were opened to 92°, was examined and found to be 23.6 kcal mol^{-1} more stable than trapezoid VIIId (but still less stable than rectangle VIIIb). Thus, it would appear that localization as represented by VIIIf was favored in VIII as a model type II structure. Analysis of the charge distributions, π-bond orders, and p_z orbital electron densities suggest that VIIIg contributes more strongly to VIII than IIIe did to III.



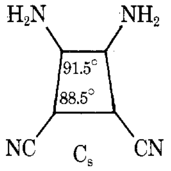
VIIIa



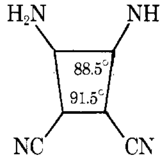
VIIIb



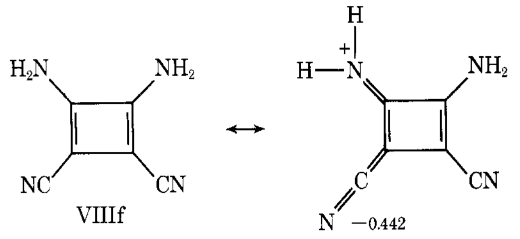
VIIIc



VIIId



VIIIe



VIIIf VIIIg

Next, the stabilities of the model donor–acceptor diaminodicyanocyclobutadienes of type I and II were compared in various geometries. In all comparisons, the type I molecules were more stable than their type II counterparts. Thus, IIIa, IIIb, and IIId were more stable than VIIIa, VIIIb, and VIIIc by 91.3, 71.0, and 90.6 kcal mol^{-1}, respectively. The greater stability of IIIa vs. VIIIa agrees with the predicted thermodynamic stabilities of Hoffman. However, it must be remembered that IIId is the favored geometry of III and VIIIb for VIII. Since IIId is more stable than VIIIb, we predict (within the limits of INDO theory) that type I molecules will be thermodynamically more stable than type II.

Questions concerning a rigorous comparison of MINDO/2 and INDO methods still exist. Currently, it is not clear if INDO and MINDO/2 results differ because previous MINDO/2 studies[7] failed to use optimized geometries or because the methods inherently differ.

Finally, it might be expected that type I cyclobutadienes, with strong donor and acceptor groups, will have D_{2h} parallelogram geometries in the gas phase and possibly in the solid phase. Carefully performed electron diffraction, microwave spectroscopy, and X-ray crystallographic studies on such molecules are needed to test this prediction. Already, one interesting study is available. Rausch et al.[19] found that the cyclobutadienyl ring, in (π-C_5H_5)-[*trans*-diphenyldi(trimethylsilyl)cyclobutadiene]cobalt, was planar with the four C–C distances equal. However, the internal angles were not 90°. Instead, a parallelogram geometry with 88.1° (at site of phenyl groups) and 91.8° (at site of silicons) was found.

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Registry No.—III, 55208-71-4; IV, 55208-72-5; V, 55208-73-6; VI, 25723-65-3; VII, 55208-74-7; VIII, 55208-75-8.

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