247. Conjugative Stabilization in an "Antiaromatic" System: The Conformational Mobility of 1,5-Bisdehydro[12]annulene[1])

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Summary

The isodynamical interconversion between the quasiplanar equilibrium conformers **1b** and **1c** of 1,5-bisdehydro[12]annulene requires a free energy of activation $\Delta G^{\ddagger} = 4.5 \pm 0.2$ kcal/mol (120 K) which was determined by line shape analysis of its temperature-dependent NMR. spectrum. Force field calculations indicate that this barrier reflects the energy needed to disrupt the cyclic π-conjugation in going to the nonplanar transition state **1a**.

Introduction. - The latest development in the battlefield of "resonance energy" has been the definition of an aromaticity index which derives solely from the topology of a given π-system [3]. While this procedure removes the arbitrary parametrization of previous schemes, the question remains, if and how the fictitious quantities so obtained relate to observable properties of chemical interest such as heats of formation, reactivity, rotational barriers, and chemical shifts [4]. It has been pointed out before [5] that the "antiaromaticity" ascribed to [4n]annulenes by relation to hypothetical polyenic reference structures does not imply that an actual disruption of the cyclic conjugation would tend to stabilize the systems. Experimental values for the energy requirements of such a process may be sought in the large amount of data concerning the conformational mobility of annulenes and dehydroannulenes [6-8]. Unfortunately, the geometrical constraints in small- and medium-sized ring systems ($n \leqslant 3$) usually impose dominant energy contributions from angular strain and non-bonded repulsions on the observable activation barriers and obscure the contributions due to conjugation in cyclic 4n- and (4n+2)-systems. Molecular models suggest that the former effects should be of less importance in 1,5-bisdehydro[12]annulene (**1**), both giving some preference to the nonplanar structure **1a** in which the *trans* double-bond is perpendicular to the mean

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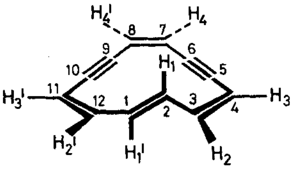
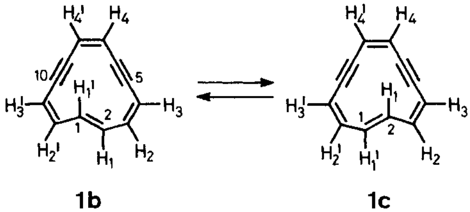
[1]) Electronic structure and photophysical properties of planar conjugated hydrocarbons with a 4n-membered ring, part III; Part II [1], part I [19]. Conformational analysis, part 135; Part 134 [2].

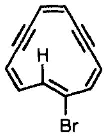
plane of the ring. In fact, there is strong evidence (see small print below) that **1** is present in solution as a rapidly equilibrating mixture of essentially planar conformers **1b** and **1c**. This can be attributed .to the conjugative stabilization of the planar form. We have measured the activation energy for the isodynamical interconversion **1b** ⇄ **1c** by low-temperature NMR. in order to estimate the magnitude of this stabilization. Force field calculations have been carried out in an effort to understand the observations in detail.



1a



1b **1c**



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The H-NMR. spectrum of **1** was first presented in 1963 by *Sondheimer* [9] and has since been the subject of numerous interpretative discussions [6] [10-15]. It clearly displays the presence of a twofold symmetry element partitioning the eight protons into four pairs of chemically equivalent nuclei. Hence, **1** was originally [9] [10] assumed to have a nonplanar equilibrium conformation of C_2 symmetry (**1a**). A little later, *Pople* [11] [16], *Kuhn* [17], and *Longuet-Higgins* [18] independently developed theoretical models predicting strong downfield shifts of the inner protons of [4n]-annulenes due to induced paramagnetic ring currents. The unusual low-field resonance (δ 10.9 ppm) of the (H_1, $H_{1'}$) hydrogen atoms attached to the *trans* double-bond of **1** was thus interpreted [11] [12] as an average value arising from rapid interchange of the inner (δ *ca.* 16.4) and outer (δ *ca.* 5.4 ppm) position in the planar equilibrium conformers **1b** and **1c**. Strong support for this hypothesis was provided by the observation of the low-field resonance (δ 16.4 ppm) of the inner proton in the bromo-derivative **2** [13]. Further evidence for the near planarity of **1** in solution and in the gas phase comes from the close similarity of the UV./VIS. and of the PE. spectra of **1** and trisdehydro[12]annulene **3** [19].

Results. - The room-temperature ("mobile") H-NMR. spectrum of **1** shown in *Fig. 1* is similar to those of *Sondheimer et al.* [10] [12] but displays some additional transitions of very weak intensity belonging to the multiplets at δ 5.02 and 11.06 ppm, respectively. It was analysed with the aid of a LAOCOON II eight-spin computer program. The coupling constants and chemical shifts used to reproduce the experimental spectrum (rms error 0.2 Hz) are given in *Table 1*. The values attributed to couplings with the protons H_4 and $H_{4'}$ may be questionable but do not affect the analysis of the triene subunit. The absence of a significant coupling between H_1 and H_3 is presumably due to the near cancellation of $^4J_{13} \cong +1$ Hz and $^4J_{13} \cong -1$ Hz in the conformations **1b** and **1c**, respectively. Couplings across more than four bonds were neglected except those across a triple bond. The coupling constants within the triene subunit differ considerably from those derived by *Sondheimer* [10] by a first-order analysis of his spectrum. In particular, the low value

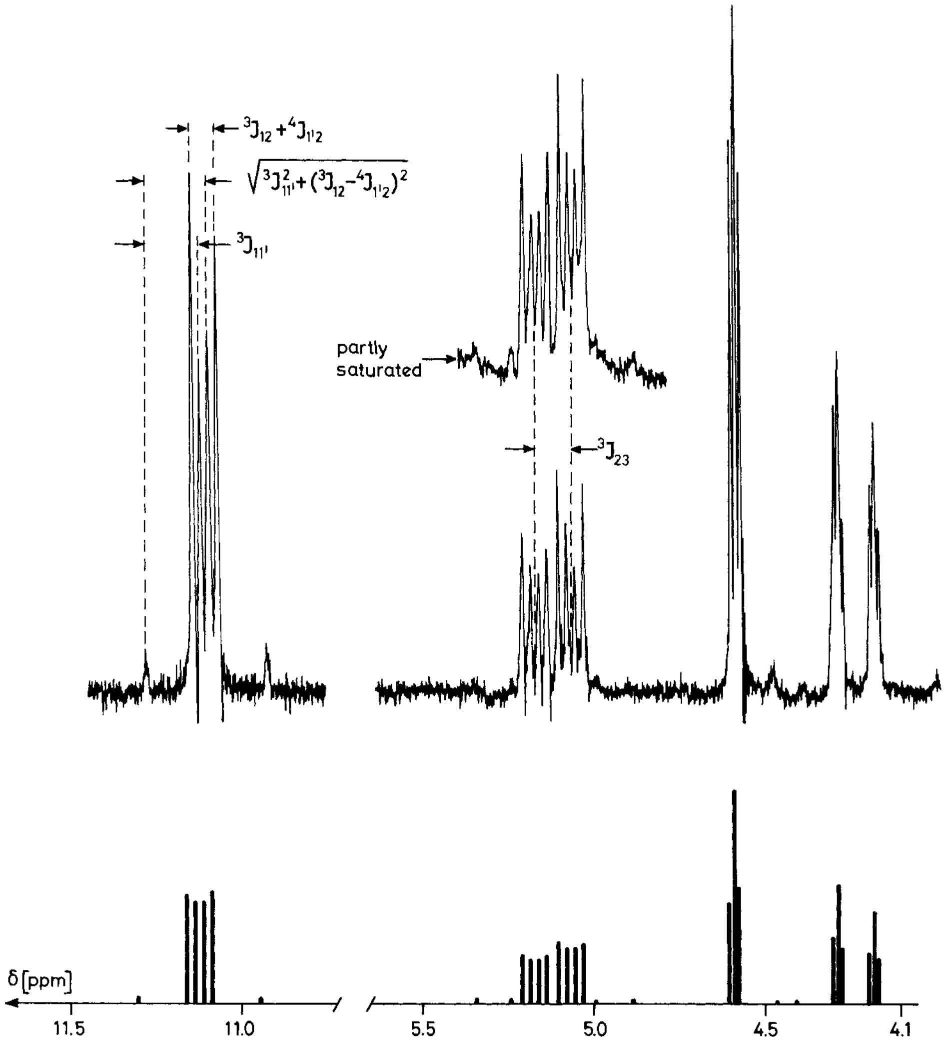

Fig. 1. *Room temperature H-NMR. of* **1** *in $CHCl_2F/CHClF_2$ 2:1.* Vertical bars indicate computer simulated spectrum. The multiplet at δ 11.12 ppm is well approximated as the *A,A'* part of an *AA'XX'* system.

of $^3J_{12} \cong 5$ Hz [10] was interpreted by *Haddon* to "reflect a substantial deviation from planarity" [15] in the equilibrium conformations of **1**. However, the system does not comply with the conditions for first-order analysis (the primed and unprimed hydrogen atoms are chemically but not magnetically equivalent) and the coupling constants given in *Table 1* are quite compatible with the expectations for a dynamic equilibrium between two nearly planar conformers.

Upon cooling the solution to −100° the only change observed in the NMR. spectrum of **1** was a gradual downfield shift of the (H_1, $H_{1'}$) resonance from

Table 1. *Chemical shifts δ (ppm) and coupling constants* J *(Hz) used in computer simulation of the H-NMR. of* **1**

H_1 $H_{1'}$	H_2 $H_{2'}$	H_3 $H_{3'}$	H_4 $H_{4'}$	$^3J_{11'}$	$^3J_{12}$ $^3J_{1'2'}$	$^4J_{1'2}$ $^4J_{12'}$	$^3J_{23}$ $^3J_{2'3'}$	$^3J_{44'}$	$^5J_{34}$ $^5J_{3'4'}$
11.122	5.117	4.236	4.590	16.6	8.4	− 1.1	10.7	12.1[a])	2.6[a])

[a]) Uncertain.

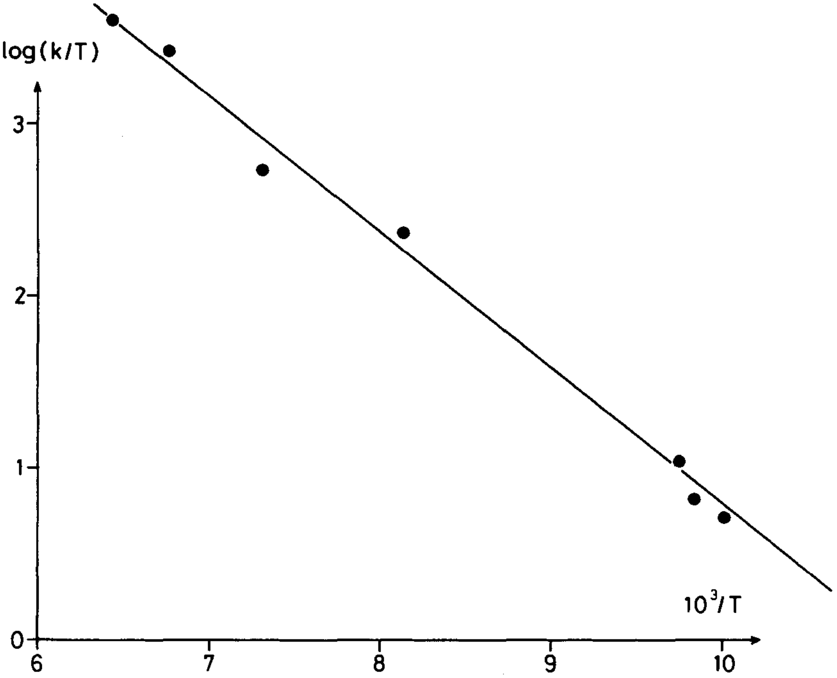

Fig. 2. *Temperature dependence of the (***1b** ⇄ **1c***)-interconversion rate constant* k

δ 11.1 to δ 11.3 ppm.[2]) This shift probably reflects the increasing degree of planarity in the lower levels of the normal modes corresponding to out-of-plane wagging and eventual rotation of the *trans* double-bond moiety. Further cooling resulted in a selective broadening of the (H_1, $H_{1'}$) multiplet and a complicated change in the fine structure of the (H_2, $H_{2'}$) multiplet. Below − 150° the former peak was lost in the baseline until at − 165° a broad signal appeared near 17.6 ppm which sharpened upon further cooling. Cooling below − 175°, where the peak had a width at half height of *ca.* 100 Hz, was prevented by precipitation of the sample resulting in an overall loss of resolution. The predicted [11] [12] strong downfield shift of the inner hydrogen atom ($H_{1'}$ in **1b** and H_1 in **1c**) has thus been verified. Unfortunately the corresponding signal of the outer hydrogen atom (H_1 in **1b** and $H_{1'}$ in **1c**), expected

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[2]) A similar shift was observed by *Sondheimer* [12]. The overall broadening of his spectrum of **1** in $(CD_3)_2CO$ solution at − 80° is presumably due to a viscosity effect or partial precipitation.

to appear near 5.5 ppm, could not be detected due to the presence of strong solvent signals above 6 ppm. To simplify the spectra for quantitative line shape analysis the couplings between (H_1, $H_{1'}$) and (H_2, $H_{2'}$) were removed by double irradiation. The rate constant k of exchange between the inner and outer sites of the (H_1, $H_{1'}$) hydrogen atoms at a given temperature T was then obtained by visual fitting of the experimental line shapes with those calculated by the simple two-site equations [20]. A plot of log (k/T) *vs.* 1/T is shown in *Fig. 2.* The *Eyring* parameters obtained from the slope ($-\Delta H^{+}/4.57$) and intercept ($10.32+\Delta S^{+}/4.57$) of the linear regression line are $\Delta H^{+}=3.6\pm0.3$ kcal/mol and $\Delta S^{+}=-7.7\pm2$ e.u. corresponding to a free energy of activation at 120 K of $\Delta G^{+}=4.5\pm0.2$ kcal/mol. The quoted 90 percent confidence limits of course do not account for possible systematic errors. Note, however, that the unusually large chemical shift difference between the inner and outer sites $\delta\nu \cong 12.1$ ppm tends to make the above values reliable in spite of the relatively large uncertainties in T and $\delta\nu$.

Force Field Calculations. - The usefulness of these calculations in understanding geometries, energies, torsional barriers, and other properties in conjugated polyenes has been discussed in some detail previously [21-24]. Simple acetylenes have also been previously studied [25], but not conjugated acetylenes. A small extension of the existing force field[3]) (1973 force field) was therefore required to include the latter class of compounds, and was straightforward. Acetylene, dimethylacetylene, diacetylene and vinylacetylene were used to establish the appropriate constants for the force field, and the bond-order, bond-length relationships for ($C_{sp}-C_{sp}$)- and ($C_{sp}-C_{sp^2}$)-bonds. The necessary equations are given in (1) and (2).

$$l_{C_{sp^2}-C_{sp}} = 1.480 - .176\,p \tag{1}$$

$$l_{C_{sp}-C_{sp}} = 1.448 - .238\,p \tag{2}$$

In the case of a conjugated diacetylene, only the "primary conjugated system" is counted in determining p (which will have a value between 0 and 1). The second (orthogonal) conjugated system is neglected in using eq. (2)

The interesting question of the torsional barrier in divinylacetylene was also considered. While it is clear that there will be no torsional barrier about the formally single bond in vinylacetylene, it is not clear that this will also be true in divinylacetylene. Accordingly, we carried out an *ab initio* calculation (STO-3G) using the Gaussian 70 program [26], assuming a standard geometry and rigid rotation. It was found that the energies of the three extreme forms (with the two vinyl groups oriented either *cis*, *trans* or at 90°) was the same within 0.6 kcal/mol[4]). We concluded

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[3]) The program (MMPI) represents an extension of the program for non-conjugated systems (MMI), and it has been submitted to the *Quantum Chemistry Program Exchange* (University of Indiana, Bloomington, Indiana, 46202) for distribution.

[4]) The bond lengths and angles assumed were (in order) 1.347, 1.429 and 1.221 Å (1.090 for CH), and 117.07 and 180°. The HCH (terminal) was 119.14°. The calculated total energies (0°, 45°, 90°, 180°) were *(Hartrees):* −227.7471, −227.7466, −227.7461 and −227.7471.

that there is no (or at least a negligible) rotational barrier in such a system, and we parameterized the program accordingly.

Using this force field, the structures and energies of the conformations of **1** were studied. The calculation was carried out; (*i*) restricting the molecule to exact planarity; (*ii*) starting near planarity and letting the molecule locate its own minimum of energy without restrictions or symmetry restraints; (*iii*) constraining the molecule to have a C_2 axis of symmetry thus forcing the central double bond to be at right angles to the mean plane of the molecule.

The planar conformation (**1b**), favoured torsionally, is destabilized by unfavourable ring angles at 2-3-4 (129.0°), 3-4-5 (127.0°), 9-10-11 (170.0°), 12-1-2 (127.3°). The average (C-C_{sp2}-C)-ring-angle is 123.9° and average deviation from trigonal is 4.3°. The internal hydrogen atom ($H_{1'}$) has severe repulsions with C(5) and C(10), amounting to 4 kcal/mol.

If the planarity constraint is removed, the molecule relieves some unfavourable ring angles and *van der Waals* interactions by rotating the C_1, C_2 double bond out of the plane of the ring. A minimum energy conformation is reached when the increase in torsional energy across ω (1-2-3-4) and ω (11-12-1-2) (due to π-bond disruption) exceeds the bond-angle and *van der Waals* stabilization. This minimum energy occurs when the dihedral angles of these butadiene-type linkages are 23.1° and 159.0°, respectively (average deviation from planarity of 21.6°). The average (C-C_{sp2}-C)-ring-angle is reduced to 122.7° with an average deviation from trigonality of 3.2°. The $H_{1'}$-repulsions are reduced by almost 3 kcal/mol. This conformation (**1b'**) is 1.03 kcal/mol more stable than the planar (**1b**).

The calculations were also carried out on conformation **1a**, assumed to be a transition state for the interchange of H_1 and $H_{1'}$. In this conformation ring-angle strain is wholly relieved. The average (C—C_{sp2}—C)-angle is 120.3° with an average deviation of 0.6° from trigonality. *Van der Waals* interactions of H_1 and $H_{1'}$ are also at a minimum. The stabilization due to these two potentials is 10.2 kcal/mol relative to the planar conformation. Offsetting this, however, is the disruption of the C_2, C_3 and C_1, C_{12} butadiene-type bonds. This causes a 20 kcal/mol destabilization of the orthogonal form. As a result, **1a** is 9.3 kcal/mol less stable than **1b**, the planar conformation.

The potential function describing the rotation of the C_1, C_2 double bond is shown in *Figure 3*. The ΔH^{+} of 3.60 kcal/mol from the low temperature NMR. work corresponds to the enthalpy difference between **1b** and **1a**. The interconversion of enantiomers (**1b'**) is not observed. The small energy maxima corresponding to a planar system may be an artifact of the force field. It is known [27] that the hydrogen atoms in this force field are a bit too "hard".

For comparison with experiment, the ΔG^{+} values are probably better than the other thermodynamic parameters. A consideration of the entropies of symmetry and mixing indicates that ΔS^{+} should be zero here, and therefore the calculated ΔG^{+} is 9.3 kcal/mol. The experimental value for ΔG^{+} is 4.5±0.2 kcal/mol. (The large negative entropy value measured experimentally appears to indicate something unexpected is occurring, or the experimental error is substantially larger than thought). While the discrepancy between the calculated and experimental value is

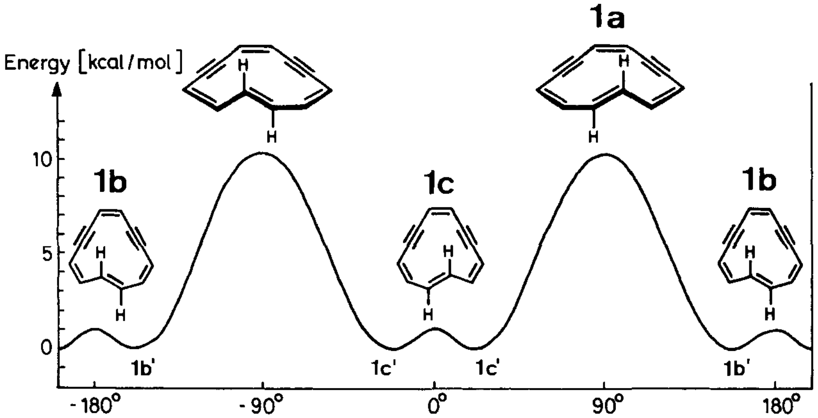

Fig. 3. *Reaction profile for rotation of the* trans *(C_1,C_2) double-bond moiety, as predicted by force field calculations*

sufficient to be disappointing, it is clear from both calculation and experiment that the form in which the double bond is twisted orthogonal to the remainder of the system corresponds to an energy maximum, and not to an energy minimum. Since the cyclic conjugated π-system of the planar molecule contains 12 electrons, it may be classified as anti-aromatic. There is some misunderstanding in the literature about anti-aromatic systems [5]. A conjugated linear polyene has a certain energy which is well approximated as an additive function of bond energies, and whether one wants to consider that this contains a conjugation energy or not is immaterial. Following *Dewar*'s definition [3], a planar, strainless cyclic polyene is anti-aromatic, if its heat of formation is higher than that calculated by summing up "polyene" bond energies. That does not mean there is an advantage for the molecule to be non-planar. Cyclooctatetraene is anti-aromatic and non-planar. It does not pucker to relieve anything unfavourable about the π-system, however. The π-system has a minimum of energy when it is planar, and puckering the system increases the π energy. Cyclooctatetraene puckers simply because the σ-system is more comfortable in the puckered form. In the present molecule, the π-system again has a lower energy when it is planar. But the other forces acting, angle strain and *van der Waals* repulsion in particular, are tending to twist the double bond out of the plane. In this case, the π-system dominates (contrary to cyclooctatetraene), so the system here is planar, or at least very nearly so.

The most uncertain part of the MMPI method is in the evaluation of torsional parameters. The values assigned to torsional constants are based in large part on the validity of our VESCF calculation as applied to non-planar π-systems. The overlap between non-parallel p-orbitals is scaled down by the cosine of the angle between the orbitals. For moderate deviations from planarity, as might be encountered in the paracyclophanes, this might be a reasonable approximation. For large deviations, as in **1a** where the p-orbitals are almost orthogonal, hyperconjugation or mixing of the σ-orbitals may become significant. At the moment, all we can do is recognize this limitation and be somewhat wary of the MMPI results for severely distorted π-systems.

Experimental Part. - 1,5-Bisdehydro[12]annulene (**1**) was obtained as a by-product in the synthesis of 1,5,9-trisdehydro-[12]annulene (**3**) by the procedure of *Untch & Wysocki* [16] when air oxygen was excluded in the last step. It was purified by column chromatography and vacuum sublimation. A two to one mixture of $CHCl_2F$ and $CHClF_2$ was used as a solvent to record the H-NMR. spectra of **1** in a sealed, degassed NMR. tube from 35 down to $-175°$. The instrument (*Varian* HA-100 A) was locked on the high-field transition of the doublet due to $CHCl_2F$ which was taken to lie at δ 7.20 ppm relative to TMS. The temperature was monitored before and after recording each spectrum by replacing the sample with a similar tube containing a calibrated *Degussa* Pt-100 thermoresistor. Temperature readings were constant within ± 1° for a given setting of the cooling system.

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REFERENCES

[1] *J. Wirz* in 'Excited States in Organic Chemistry and Biochemistry', Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. X (B. Pullman, N. Goldblum, eds.), p. 283, Reidel 1977.
[2] *N. L. Allinger, L. Dosen-Micovic, J. F. Viskocil jr. & M. T. Tribble*, in press.
[3] *J. Aihara*, J. Amer. chem. Soc. *98*, 2750 (1976); *I. Gutman, M. Milan & N. Trinajstić*, ibid. *99*, 1692 (1977).
[4] A provocative discussion of this topic is found in the comments by *E. Heilbronner* in 'Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity', Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. III (E. D. Bergmann & B. Pullman, eds.), Jerusalem 1971.
[5] *C. J. Finder, D. Chung & N. L. Allinger*, Tetrahedron Letters *1972*, 4677.
[6] *I. C. Calder & P. J. Garratt*, J. chem. Soc. *B 1967*, 660.
[7] *J. F. M. Oth*, Pure appl. Chemistry *25*, 573 (1971).
[8] *F. Sondheimer*, Accounts chem. Res. *5*, 81 (1972).
[9] *F. Sondheimer*, Pure appl. Chemistry *7*, 363 (1963).
[10] *R. Wolovsky & F. Sondheimer*, J. Amer. chem. Soc. *87*, 5720 (1965).
[11] *J. A. Pople & K. G. Untch*, J. Amer. chem. Soc. *88*, 4811 (1966).
[12] *F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent & R. Wolovsky*, Chem. Soc. spec. Publ. No. *21*, 75 (1967).
[13] *K. G. Untch & D. C. Wysocki*, J. Amer. chem. Soc. *89*, 6386 (1967).
[14] *H. A. Staab & R. Bader*, Chem. Ber. *103*, 1157 (1970); *H. A. Staab & P. Gunthert*, ibid. *110*, 619 (1977); *H. A. Staab & H. J. Shin*, ibid. *110*, 631 (1977).
[15] *R. C. Haddon, V. R. Haddon & L. M. Jackman*, Fortschr. chem. Forsch. *16*, 103 (1971).
[16] See also footnote 9 in *K. G. Untch & D. C. Wysocki*, J. Amer. chem. Soc. *88*, 2608 (1966).
[17] *F. Baer, H. Kuhn & W. Regel*, Z. Naturforsch. *A 22*, 103 (1967).
[18] *H. C. Longuet-Higgins*, Chem. Soc. spec. Publ. No. *21*, 109 (1967).
[19] *J. Wirz*, Helv. *59*, 1647 (1976).
[20] *H. S. Gutowsky & C. H. Holm*, J. chem. Physics *25*, 1228 (1956); *H. Günther*, 'NMR-Spektroskopie', Georg Thieme Verlag Stuttgart 1973.
[21] *N. L. Allinger & J. T. Sprague*, J. Amer. chem. Soc. *95*, 3893 (1973).
[22] *A. Warshel & M. Karplus*, J. Amer. chem. Soc. *94*, 5612 (1972); *A. Warshel*, Modern theoretical Chemistry *7*, 133 (1977).
[23] *N. L. Allinger*, Adv. physic. org. Chemistry *13*, 1 (1976).
[24] *H. J. Lidner*, Tetrahedron *30*, 1127 (1974).
[25] *N. L. Allinger & A. Y. Meyer*, Tetrahedron *31*, 1087 (1975).
[26] *L. Radom & J. A. Pople*, J. Amer. chem. Soc. *92*, 4786 (1970); The program (Gaussian 70) was obtained from QCPE (Footnote 3), program number 236.
[27] *N. L. Allinger*, J. Amer. chem. Soc., in press.