

The Crystal and Molecular Structure of the 1-Carbomethoxy Derivative of 5,7,12,14,16(4)-Tetracyclo[9,2,2,1^{4,11},0^{8,16}]hexadecapentaene, with ¹H and ¹³C N.m.r. Studies of Ring Inversion and Strain-Energy Calculations*

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The title compound, C₁₈H₁₈O₂, is a derivative of an acetylation product of [2,2]metaparacyclophane. It forms colorless prisms belonging to the space group $P2_1/n$, with four molecules in the unit cell (two enantiomeric pairs). The cell parameters are $a = 14.118$, $b = 5.986$, and $c = 16.738$ Å, $\beta = 97.38^\circ$. A Picker automated diffractometer was used to collect data, with Cu $K\alpha$ radiation and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares calculations with 2051 measured structure factors to a final R index of 0.050. The chiral conformation of the eight-membered ring and the boat-shaped cyclohexadiene ring are prominent features of the molecular geometry. Most bond angles and distances are normal; a few are markedly affected by intramolecular crowding. The two enantiomers in the crystal are consistent with the extreme forms of an internal motion which results in an apparent plane of symmetry in the molecule at room temperature; they also conform well to low-temperature ¹H and ¹³C n.m.r. spectra and to the structure calculated by strain-energy minimization techniques. The calculated barrier height to ring inversion of 11.5 kcal mol⁻¹ compares well with the free energy of ring inversion of 9.2 kcal mol⁻¹ determined from n.m.r. measurements. In keeping with the relatively high barrier to internal motion of the molecule in solution, the carbon skeleton in the crystal seems to be well represented as a librating rigid body.

Introduction

In studies of barriers to ring rotation in [2,2]metaparacyclophane (I) and its derivatives, Hefelfinger & Cram (1971) found that acetylation of (I) yielded the expected 12-acetylmethaparacyclophane, (II), only in minor amounts, while the major product, (III), did not exhibit the chemical and spectral characteristics of a paracyclophane. The ¹H n.m.r. spectrum of the major product was consistent with a plane of symmetry passing through either a *p*-substituted benzene ring or a diene. If this product were a metaparacyclophane derivative, it would have to be considerably distorted to produce a conformation with a plane of symmetry through the *para* ring. These observations prompted the present structural study.

Several derivatives were made from the original methyl ketone, (III), in the early attempts to deduce its structure. The most promising crystals for X-ray work were obtained from the methyl ester of the carboxylic acid prepared by KOBr oxidation of (III). This ester (IV) has the composition C₁₈H₁₈O₂. The crystal study was begun before the characterization of the compound had been completed; however, its results confirmed the structure deduced from chemical and spectral evidence.

A stereoscopic view of the molecule is shown in Fig. 1; Fig. 2 shows the atom numbering scheme. The systematic name of the hydrocarbon skeleton of (IV) is 5,7,12,14,16(4)-tetracyclo[9,2,2,1^{4,11},0^{8,16}]hexadecapentaene (V).

Experimental

Colorless transparent rods of (IV) were grown from an ether-pentane solution by D. Hefelfinger. Oscillation, rotation and zero-level Weissenberg photographs indicate that the crystal class is monoclinic with **b**, the unique axis, being the needle axis. Systematic absences, determined from *h0l*, *h1l*, and *h2l* Weissenberg photographs, are: *h0l*: $h+l=2n+1$, and *Ok0*: $k=2n+1$. The space group is thus determined to be $P2_1/n$; representation as $P2_1/c$ leads to an inconveniently large β , 138°.

The crystal chosen for data collection was a needle, 0.63 mm long, with trapezoidal cross section about 0.45 by 0.36 mm. The effective radius for absorption varied therefore from about 0.18 to about 0.27 mm. The absorption coefficient, μ , for Cu $K\alpha$ radiation is 0.65 mm⁻¹ for four molecules of C₁₈H₁₈O₂ per unit cell. The maximum variation in corrected values of $|F_{\text{obs}}|$ would thus be about 5%. No absorption corrections were made.

Lattice parameters were determined by centering a number of reflections on a manual diffractometer and refining the approximate parameters so obtained by least-squares calculations based on 2θ values. The radiation used was Cu $K\alpha$, the parameters are $a = 14.118$ (2), $b = 5.986$ (1), $c = 16.738$ (2) Å, and $\beta =$

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97.38 (1)°. The volume of the unit cell is 1402.5 Å³. The calculated density for four molecules per unit cell and a molecular weight of 266.26 is 1.262 g cm⁻³. The density measured by flotation in zinc iodide solution was 1.266 (5) g cm⁻³.

The intensities of approximately 2400 unique reflections (a complete quadrant of reflection to about 130° in 2θ) were measured on a Picker manual diffractometer with Cu $K\alpha$ radiation. The structure was solved and partially refined with these data. A second set of data, collected with a Picker FACS-1 automatic diffractometer with the same crystal, included 2278 unique intensities to about $2\theta=127^\circ$. Cu $K\alpha$ radiation (wavelength 1.5418 Å), which had been monochromatized with a graphite crystal, was used. The takeoff angle was about 2.5°; diffraction maxima were scanned in the $\theta-2\theta$ mode at a constant rate of 1° (2θ) min⁻¹. Scan widths were 1.7 to 2.6° as necessary to include the entire peak. Background counts were measured for 10 s before and after each scan. This second data set was used in the final refinement of the structure.

The program *UCFACS* (Duesler & Raymond, 1971), adapted by John Bell and Michael Murphy, was used for data reduction. Solution of the structure was accomplished with a direct-methods program (Long, 1965), and refinement was carried out with *FMLS1* (Gantzel, Sparks & Trueblood). Drawings and molecular geometry calculations were carried out with the Oak Ridge programs *ORTEP* and *ORXFFE*. Rigid-body parameters were calculated with *TLS* (Schoemaker & Trueblood, 1968). The strain-energy calculations were made with *MOLBD2* (Boyd, 1972).

Nuclear magnetic resonance spectra were obtained on a spectrometer equipped with a superconducting solenoid operating at 59 kG (Anet, Basus, Bradley & Cheng, 1971). The 251 MHz ¹H n.m.r. spectra were recorded by computer-controlled digital sweeps, while the 63.1 MHz ¹³C spectra represent Fourier transforms of the sum of several hundred free-induction decays that were initiated by *ca* 20 μs radiofrequency pulses. In the ¹³C spectra, off-resonance single-frequency proton decoupling was used for assignment purposes; otherwise noise decoupling of protons was employed.

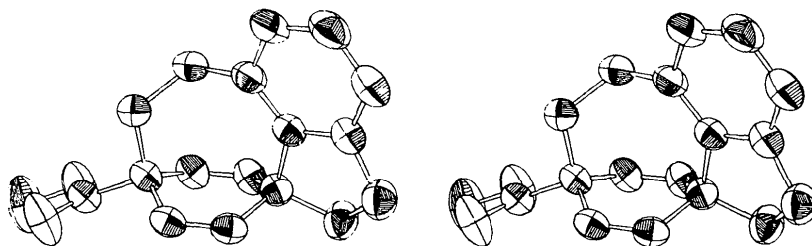


Fig. 1. Stereoscopic view of the molecular structure of (IV). Hydrogen atoms are not shown. The thermal ellipsoids are scaled to enclose 50% probability. The two oxygen atoms in the methoxycarbonyl group are represented by unshaded ellipsoids.

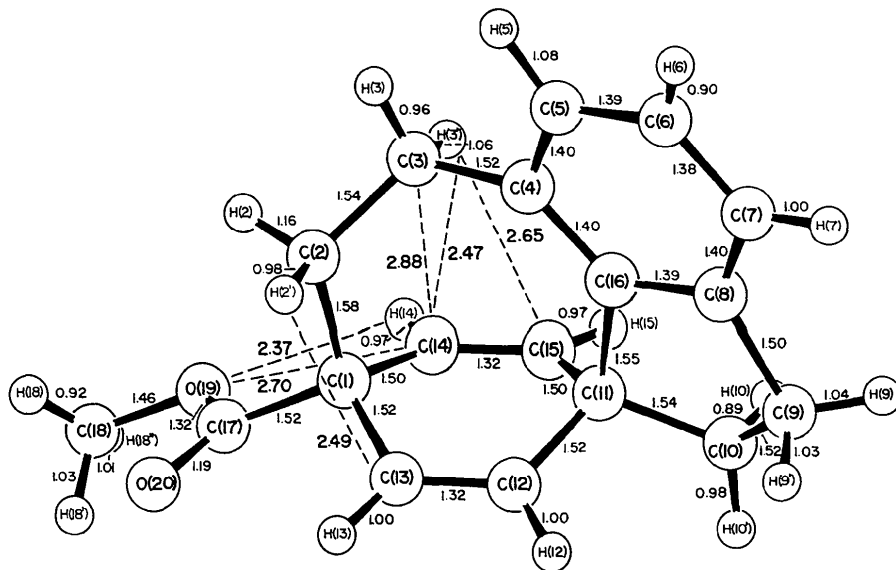


Fig. 2. Perspective view of the molecule (IV). Atom numbers correspond to the position parameters in Table 2(a) and (c). Bond lengths and most important intramolecular distances are, for clarity, given only to the nearest hundredth of an Å; more precise values are given in Table 3.

Nuclear magnetic resonance study

Information on the structure of (IV) in solution was sought from n.m.r. spectroscopy, as this technique can yield conformational energy barriers which lie in the range 5 to 25 kcal mol⁻¹ (Anet & Anet, 1971). The ¹H and ¹³C n.m.r. spectra of (IV) dissolved in carbon disulfide were obtained over the temperature range -120 to 25°C (Figs. 3 and 4). Both the ¹H and ¹³C spectra show broadening effects at about -50 to -90°C and it is clear that some conformational process in (IV) becomes slow on the 'n.m.r. time scale' below about -100°C.

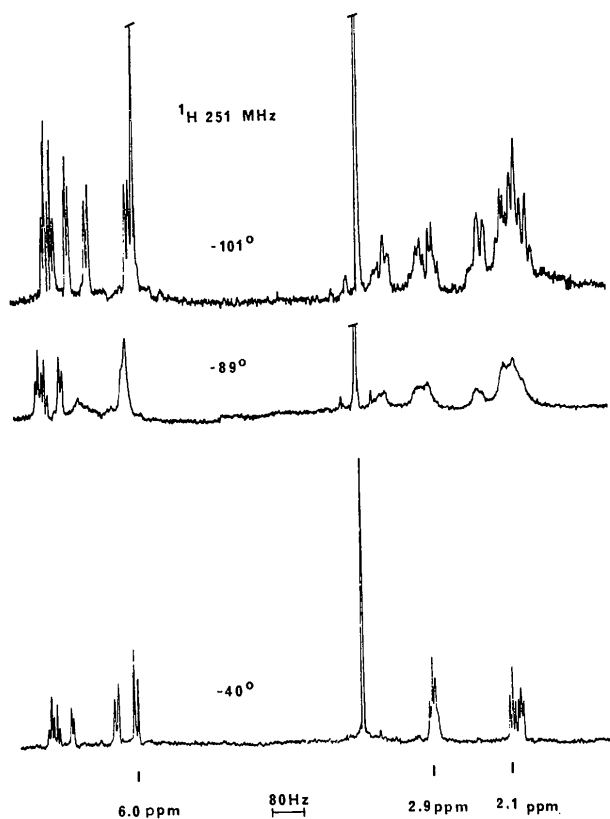


Fig. 3. 251 MHz ¹H n.m.r. spectra of compound (IV) as a 1% solution in CS₂. The chemical shift scale refers to p.p.m. downfield from internal tetramethylsilane.

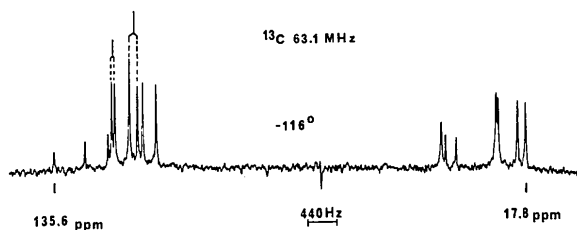


Fig. 4. 63.1 MHz ¹³C n.m.r. spectrum of compound (IV) as a 2% solution in CS₂ at -116°. The dotted lines indicate the ethylenic carbon peaks which coalesce at higher temperatures. The chemical shifts are p.p.m. downfield from internal tetramethylsilane.

The ¹H spectrum of (IV) at -40° and above can be interpreted in terms of two mirror-image structures (see Fig. 2 for one enantiomer), that are interconverting rapidly by a ring-inversion process. The lowest-field resonances (6.6 to 6.9 p.p.m.) in Fig. 3 can be assigned to aromatic protons on the basis of their chemical shifts and splitting patterns (a triplet and two doublets). The triplet belongs to the central proton on the aromatic ring as the splitting indicates a coupling to two *ortho* protons. The two doublets at 6.0 to 6.2 p.p.m. correspond to a total of four protons and arise from two like pairs of *cis* olefinic protons. The presence of only two chemical shifts for these protons is consistent with fast ring inversion, although it could also be due to an accidental shift equivalence. The line at 3.7 p.p.m. is of an intensity corresponding to three protons and arises from the methyl ester group. The multiplet at 2.9 p.p.m. comes from four protons, and can be assigned to benzylic methylene groups. The two triplets near 2.1 p.p.m. also represent four protons and can be assigned to methylene groups that are not adjacent to the benzene ring.

The ¹H n.m.r. spectrum at -101° (Fig. 3) reveals chemical shifts appropriate to a static structure. In particular, there are now more than two chemical shifts for the olefinic protons; four distinct shifts are not observed because of the accidental equivalence of two resonances at 6.0 p.p.m. The benzylic methylene protons at 2.9 p.p.m. give rise to a rather complex set of bands. Four chemical shifts (2.37, 2.84, 2.96, and 3.34 p.p.m.) can be discerned and the fine structure results from spin-spin coupling within the methylene group as well as to the adjacent methylene group. Because the two different benzylic methylene groups have essentially the same chemical shifts (*ca* 2.9 p.p.m.) at -40°C, the low-temperature resonances at 2.37 and 3.34 p.p.m. (average = 2.86 p.p.m.) must be assigned to one methylene group and the resonance at 2.84 and 2.96 p.p.m. (average = 2.90 p.p.m.) must be assigned to a different methylene group. Thus the chemical shift difference within one of these methylene groups is much larger than it is in the other. The two benzylic protons in the five-membered ring, which is nearly planar, are in rather similar sites, and thus can be assigned to the bands at 2.84 and 2.96 p.p.m. This leaves the bands at 2.37 and 3.34 p.p.m. for the methylene group in the eight-membered ring, an assignment that is consistent with the very different positions of these protons with respect to the double bonds and the plane of the aromatic ring. The non-benzylic methylene proton bands change at low temperatures, but the chemical shift separations that take place are fairly small and very complex multiplets result.

The resonances of the methyl group and of the aromatic ring are unchanged between room temperature and -120°, as expected, since the environments of these nuclei are unaffected by ring inversion. Internal rotations about the single bonds in the

methoxycarbonyl group are expected to be very fast at -100°C and this group therefore behaves as though it had axial symmetry as far as its effect on the number of ring proton resonances is concerned.

The natural-abundance ^{13}C spectrum of (IV) was obtained with complete decoupling of protons and thus only ^{13}C chemical shifts are observed (Levy & Nelson, 1972; Stothers, 1972). Temperature-dependent changes are limited to mergings of olefinic resonances at 114.7 and 116.7 p.p.m., and at 120.1 and 121.0 p.p.m. (see Fig. 4). The three lowest-field lines (122.0, 127.7, and 135.6 p.p.m.) are weak and correspond to aromatic carbons that do not bear hydrogens. The aromatic C-H carbons occur at 110.0, 113.3 and 116.7 p.p.m. The high-field resonances in the ^{13}C spectrum can be assigned as follows: 38.7 (methyl); 37.7 and 35.1 (saturated quaternary carbons); 25.1 and 24.5 (benzylic CH₂ groups); 19.7 and 17.8 p.p.m. (non-benzylic CH₂ groups).

The rate constant (k , in s^{-1}) for ring inversion in (IV) can be calculated at the coalescence temperature for the benzylic methylene protons of the eight-membered ring. These protons have a large relative chemical shift ($\Delta\nu = 254$ Hz) so that the simple expression

$$k = \pi\Delta\nu/\sqrt{2}$$

may be used and coupling effects may be neglected. The value of k at -70°C is about $5.6 \times 10^2 \text{ s}^{-1}$ and the free energy for ring inversion (ΔG^{\ddagger}), calculated from the absolute rate theory with a transmission coefficient of 1, is $9.2 \pm 0.2 \text{ kcal mol}^{-1}$, where the error includes temperature uncertainties and the neglect of spin coupling. The changes observed in the ^{13}C spectra are consistent with a ΔG^{\ddagger} of about 9 kcal mol^{-1} , but no attempt to obtain rate constants from these spectra was made. Neither the ^1H nor the ^{13}C spectra are suitable for a meaningful determination of the activation energy (or ΔH^{\ddagger} and ΔS^{\ddagger}). However, it is expected that ring inversion in the present compound will have a ΔS^{\ddagger} close to zero, so that $\Delta H^{\ddagger} \approx \Delta G^{\ddagger}$.

Structure solution and refinement

Intensities measured with the automated diffractometer were corrected (Duesler & Raymond, 1971) for background radiation, and Lorentz and polarization corrections were applied; an ideally perfect monochromator crystal was assumed. Standard deviations were calculated as follows:

$$\sigma(B) = [(t/t_b) (\text{BKG})]^{1/2}$$

$$\sigma(F) = \{[C_{\text{int}} + \sigma^2(B) + (0.04C_{\text{net}})^2]/2Lp(C_{\text{net}})\}^{1/2}$$

where $\sigma(B)$ is the standard deviation of the background measurement, $\sigma(F)$ is the standard deviation of the observed structure factor, t/t_b is the ratio of peak scan time to total background counting time, BKG and C_{int} are total background and total peak counts respectively, and C_{net} is the measured intensity of the peak less the background intensity.

For 227 reflections, the net intensity was calculated to be less than 1.95 times the standard deviation of the background intensity, $\sigma(B)$; these were not used in the refinement. There remained 2051 unique reflections, not including systematic absences.

The structure was readily solved by direct methods (Long, 1965) based on Sayre's equation. Approximately 300 E values (Karle & Hauptman, 1956) ($E \geq 1.5$) were used; the set of phases with the highest consistency index and the least number of cycles required for convergence was used to calculate an E map. 19 of the 20 carbon and oxygen atoms in the structure emerged from the map in a reasonable arrangement. The final atom was located with an electron density map that had been phased with the other 19.

The structure was refined by full-matrix least-squares calculations, with atomic form factors for bonded carbon and oxygen from *International Tables for X-ray Crystallography* (1962), and for bonded hydrogen from Stewart, Davidson & Simpson (1965). Refinement with isotropic temperature factors brought the discrepancy index

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

to 0.175. The quantity minimized was

$$\sum \left(\frac{|F_{\text{obs}}| - |F_{\text{calc}}|}{\sigma(F)} \right)^2.$$

Further refinement with anisotropic temperature factors reduced the discrepancy index to 0.111. A difference electron-density map was then used to locate the 18 hydrogen atoms. All appeared on the difference map unambiguously, with the exception of the three hydrogen atoms of the methyl group, which presented somewhat diffuse peaks but could nevertheless be assigned positions. Hydrogen-atom positions and isotropic temperature factors were added to the refinement, resulting in the reduction of the R index to 0.08. Up to this point manual diffractometer data had been used in the analysis.

Two cycles of least-squares refinement with the second set of data reduced the R index further to 0.068. For many strong reflections, $|F_{\text{obs}}|$ was significantly smaller than $|F_{\text{calc}}|$, by an average of about 20%, so a secondary extinction correction (Zachariasen, 1963; Zachariasen & Plettinger, 1965) was applied. The extinction coefficient, C , was 1.370×10^{-5} , and the maximum correction was a factor of 1.27 in $|F_{\text{obs}}|$ for the $\bar{2}10$ reflection. Two cycles of refinement subsequent to the secondary extinction correction resulted in very small parameter shifts (0.2–0.3 e.s.d.), and a final R value of 0.050.* The final figure of merit, the square

* Table 1, the observed and calculated structure factors, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30754 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

root of the weighted sum of residuals divided by the number of independent observations minus the number of parameters, was 3.54. This rather large figure suggests that the $\sigma(F)$ may be artificially small. Since an analysis of the variation of the weighted sum of the squares of the residuals with $\sin \theta/\lambda$ showed no perceptible trend, the figure of merit suggests that all $\sigma(F)$ should be increased by a factor of 3.5. If this were done, the value of $\sigma(F)$ for very weak reflections would be about 1.4, and the only one of the 227 zero-weighted reflections* for which $|F_{\text{calc}}|$ would exceed $2\sigma(F)$ would then be $-3,2,18$ ($|F_{\text{calc}}| = 5.0$). The e.s.d. of the electron density is about $0.04 \text{ e } \text{Å}^{-3}$.

Molecular geometry and packing

Final atomic positions and thermal parameters are listed in Table 2. Tables 3 and 4 give bond lengths, short intramolecular non-bonded distances, bond angles and least-squares planes of interest. Fig. 2 shows the numbering scheme and important intramolecular distances. In Fig. 5, the two enantiomers are viewed from a position above the cyclohexadiene ring, the special properties of which posed the original structural problem. Internal bond angles and torsion angles that define ring conformations are illustrated in

* All reflections required to be extinguished by the space-group symmetry had measured intensities less than $1.95 \sigma(B)$, except for 302, for which $|F_{\text{obs}}|$ was about 2.8. It can be shown that this anomaly is attributable to double diffraction involving the two strong reflections $1\bar{1}0$ and -412 .

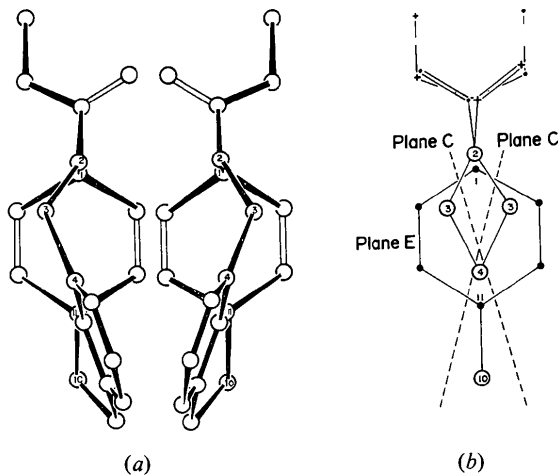


Fig. 5. The two enantiomers of (IV). (a) Perspective view; the two enantiomers are placed side by side and viewed looking down on the plane of the four olefinic carbon atoms in the cyclohexadiene (plane E, Table 4). (b) The two enantiomers are superimposed in outline (carbon atoms 5, 6, 7, 8, 9, and 16 are removed for clarity). The dashed lines indicate the projections of the planes (C in Table 4) through the five- and six-membered rings in the two enantiomers (the rings are not themselves shown). The average position of these two planes would lie on a mirror plane through atoms C(1) and C(11) in the cyclohexadiene, and nearly through atoms C(2), C(4) and C(10).

Table 2. Final parameters

Estimated standard deviations of the least significant digits appear in parentheses.

(a) Atomic position parameters ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	1016 (1)	-1402 (3)	3721 (1)
C(2)	22 (1)	-356 (4)	3856 (1)
C(3)	770 (1)	-420 (5)	3132 (1)
C(4)	-699 (1)	996 (4)	2392 (1)
C(5)	-1431 (2)	2524 (5)	2154 (1)
C(6)	-1460 (2)	3778 (5)	1456 (2)
C(7)	-762 (2)	3543 (4)	960 (2)
C(8)	-17 (1)	2055 (3)	1181 (1)
C(9)	853 (2)	1638 (4)	778 (2)
C(10)	1285 (2)	-461 (5)	1187 (2)
C(11)	949 (1)	-532 (3)	2026 (1)
C(12)	1597 (1)	791 (3)	2641 (1)
C(13)	1625 (1)	400 (3)	3415 (1)
C(14)	877 (1)	-3264 (4)	3122 (1)
C(15)	828 (2)	-2846 (4)	2344 (1)
C(16)	8 (1)	814 (3)	1884 (1)
C(17)	1475 (1)	-2119 (3)	4555 (1)
C(18)	1803 (4)	-5075 (6)	5476 (2)
O(19)	1377 (2)	-4264 (3)	4692 (1)
O(20)	1869 (2)	-894 (3)	5047 (1)

(b) Thermal parameters ($\times 10^4$). The temperature factor is expressed as: $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	47 (1)	256 (6)	38 (1)	-8 (4)	-3 (1)	-4 (3)
C(2)	50 (1)	417 (8)	38 (1)	20 (4)	12 (2)	10 (4)
C(3)	41 (1)	489 (10)	45 (1)	-1 (5)	9 (2)	29 (5)
C(4)	43 (1)	354 (7)	41 (1)	7 (4)	-6 (1)	-13 (4)
C(5)	46 (1)	518 (10)	48 (1)	63 (5)	-11 (2)	-11 (5)
C(6)	57 (1)	436 (9)	52 (1)	103 (5)	-18 (2)	5 (5)
C(7)	68 (1)	350 (7)	44 (1)	31 (5)	-21 (2)	15 (4)
C(8)	59 (1)	286 (6)	38 (1)	16 (4)	-6 (2)	-6 (4)
C(9)	75 (1)	396 (8)	41 (1)	41 (6)	17 (2)	28 (4)
C(10)	75 (2)	397 (9)	41 (1)	85 (6)	25 (2)	5 (5)
C(11)	52 (1)	267 (6)	37 (1)	30 (4)	9 (1)	-11 (3)
C(12)	43 (1)	257 (6)	44 (1)	10 (4)	9 (1)	14 (4)
C(13)	44 (1)	244 (6)	45 (1)	-11 (4)	-2 (1)	-11 (4)
C(14)	61 (1)	236 (6)	44 (1)	-24 (4)	-6 (2)	-0 (4)
C(15)	68 (1)	249 (6)	42 (1)	8 (4)	-6 (2)	-27 (4)
C(16)	46 (1)	271 (6)	37 (1)	-2 (4)	-4 (1)	-21 (3)
C(17)	54 (1)	282 (6)	40 (1)	-10 (4)	-0 (2)	8 (4)
C(18)	179 (4)	399 (11)	47 (1)	14 (11)	-35 (4)	80 (6)
O(19)	131 (2)	304 (6)	46 (1)	-76 (4)	-33 (2)	60 (3)
O(20)	126 (2)	364 (6)	48 (1)	-72 (4)	-60 (2)	6 (3)

(c) Position parameters ($\times 10^3$) and isotropic temperature factors for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(2)	-23 (2)	111 (4)	430 (2)	5.2 (5)
H(2')	19 (2)	148 (5)	405 (2)	6.2 (6)
H(3)	-135 (2)	-3 (4)	335 (1)	5.3 (5)
H(3')	-81 (2)	205 (6)	291 (2)	7.7 (7)
H(5)	-203 (2)	272 (5)	249 (2)	6.5 (6)
H(6)	-194 (2)	474 (6)	136 (2)	8.3 (8)
H(7)	-76 (2)	440 (4)	44 (2)	6.0 (6)
H(9)	70 (2)	152 (5)	16 (2)	7.1 (6)
H(9')	128 (2)	302 (5)	87 (2)	6.6 (6)
H(10)	101 (2)	-157 (4)	89 (2)	5.6 (6)
H(10')	197 (2)	-68 (4)	118 (2)	5.7 (5)
H(12)	201 (2)	193 (5)	242 (2)	6.5 (6)
H(13)	201 (1)	133 (4)	383 (1)	4.4 (4)
H(14)	81 (2)	-478 (5)	331 (2)	5.8 (6)
H(15)	73 (2)	-401 (4)	194 (1)	5.4 (5)
H(18)	150 (2)	-447 (6)	588 (2)	7.8 (9)
H(18')	241 (4)	-414 (9)	564 (3)	14.3 (16)
H(18'')	196 (3)	-671 (8)	542 (2)	11.3 (11)

Fig. 6. A view of the packing in the unit cell is shown in Fig. 7, and short intermolecular distances appear in Table 5.

Most bond lengths are normal. The exception is the C(1)–C(2) distance of 1.58 Å, which is more than ten standard deviations longer than the comparable bonds in ethane and diamond, 1.537 and 1.544 Å. Other elongated C–C single bonds have been observed in precise structure determinations, for example 1.573 Å in 4,12-dimethyl[2,2]metacyclophane (Hanson, 1962), an average of 1.59 Å in [2,2]paracyclophane and its octafluoro derivative (Hope, Bernstein & Trueblood, 1972), 1.584 and 1.578 Å in 1-biapocamphane and 1-biadamantane (Alden, Kraut & Traylor, 1968), 1.573 Å in hexamethylethane (Bartell, 1966), and 1.611 Å in tri-*t*-butylmethane (Burgi & Bartell, 1972). Each of these elongations has been attributed to intramolecular interactions. In the present molecule, the lengthening of the C(1)–C(2) distance may result in part from short transannular contacts such as those of C(14) with C(3) and H(3') (Fig. 2). These distances cannot be increased by changes in torsion angles because of fusion with the five- and six-membered rings and the consequent rigidity of the cyclohexadiene boat. There are also transannular interactions involving C(13) and C(15) with the hydrogen atoms at C(2) and C(3) [Fig. 2 and

Table 3. *Molecular geometry*

(a) Carbon–carbon and carbon–oxygen bond distances

Estimated standard deviations of the least significant digits appear in parentheses.

	Observed distance, (uncorrected)	Observed distance, corrected* for molecular libration	Calculated distance, SE (min)†
C(1)–C(2)	1.579 (3) Å	1.585 Å	1.55 Å
C(2)–C(3)	1.539 (3)	1.542	1.55
C(3)–C(4)	1.516 (3)	1.519	1.52
C(4)–C(5)	1.399 (3)	1.401	1.40
C(5)–C(6)	1.386 (4)	1.388	1.39
C(6)–C(7)	1.374 (4)	1.380	1.39
C(7)–C(8)	1.392 (3)	1.395	1.39
C(8)–C(9)	1.497 (3)	1.503	1.50
C(9)–C(10)	1.521 (4)	1.524	1.54
C(10)–C(11)	1.540 (3)	1.544	1.55
C(11)–C(12)	1.511 (3)	1.516	1.51
C(12)–C(13)	1.313 (3)	1.316	1.34
C(13)–C(1)	1.510 (3)	1.515	1.51
C(1)–C(14)	1.496 (3)	1.502	1.51
C(14)–C(15)	1.318 (3)	1.321	1.34
C(15)–C(11)	1.502 (3)	1.505	1.51
C(11)–C(16)	1.546 (3)	1.551	1.51
C(16)–C(8)	1.388 (3)	1.391	1.38
C(16)–C(4)	1.396 (3)	1.402	1.40
C(1)–C(17)	1.523 (3)	1.525	
C(17)–O(20)	1.187 (3)	1.191	
C(17)–O(19)	1.313 (3)	1.319	
C(18)–O(19)	1.455 (4)	1.456	

* The corrected distances were calculated from treatment of the 16-atom carbon framework as a librating rigid body (see text).

† Calculated distances and angles for the structure corresponding to minimum strain energy (see text).

Table 3 (cont.)

(b) Bond angles involving carbon and oxygen atoms. Estimated standard deviation of each bond angle is 0.2°.

	Observed angle	Calculated angle, SE (min)†
C(1)–C(2)–C(3)	116.5°	115°
C(2)–C(3)–C(4)	120.8	118
C(3)–C(4)–C(5)	118.3	118
C(3)–C(4)–C(16)	125.5	125
C(16)–C(4)–C(5)	116.0	118
C(4)–C(5)–C(6)	122.3	121
C(5)–C(6)–C(7)	120.6	120
C(6)–C(7)–C(8)	118.7	118
C(7)–C(8)–C(16)	120.3	121
C(7)–C(8)–C(9)	128.5	126
C(16)–C(8)–C(9)	111.1	112
C(8)–C(9)–C(10)	103.8	103
C(9)–C(10)–C(11)	106.3	106
C(10)–C(11)–C(16)	101.8	103
C(10)–C(11)–C(12)	112.1	111
C(10)–C(11)–C(15)	114.3	112
C(12)–C(11)–C(15)	109.2	110
C(12)–C(11)–C(16)	105.3	108
C(15)–C(11)–C(16)	113.7	113
C(11)–C(12)–C(13)	121.2	120
C(12)–C(13)–C(1)	121.1	120
C(13)–C(1)–C(14)	109.7	110
C(13)–C(1)–C(17)	108.5	
C(14)–C(1)–C(17)	114.1	
C(2)–C(1)–C(17)	105.2	
C(2)–C(1)–C(13)	108.6	111
C(2)–C(1)–C(14)	110.4	111
C(1)–C(14)–C(15)	120.4	120
C(14)–C(15)–C(11)	122.1	120
C(11)–C(16)–C(8)	109.8	110
C(11)–C(16)–C(4)	127.9	129
C(8)–C(16)–C(4)	120.1	121
C(1)–C(17)–O(20)	124.6	
C(1)–C(17)–O(19)	113.2	
O(20)–C(17)–O(19)	122.2	
C(17)–O(19)–C(18)	116.3	

(c) Some short intramolecular non-bonded distances, ≤ 3.50 Å. Distances between atoms bonded to the same atom are not included, nor are H···H contacts listed. The shortest such intramolecular H···H distance is 2.19 Å [H(2)–H(3)].

	Distance	Calculated distance SE (min)†
O(20)···H(18')	2.27 Å	
O(19)···H(14)	2.37	
O(20)···H(13)	2.46	
O(20)···H(18)	2.64	
O(19)···H(2)	2.96	
C(14)···H(3')	2.47	2.46
C(13)···H(2')	2.49	2.54
C(15)···H(10)	2.60	2.57
C(15)···H(3')	2.65	2.69
O(20)···C(18)	2.61	
O(19)···C(14)	2.70	
O(20)···C(13)	2.82	
O(20)···C(2)	3.09	
O(19)···C(2)	3.23	
C(3)···C(14)	2.88	2.84
C(3)···C(15)	3.12	3.10
C(4)···C(15)	3.16	3.14
C(4)···C(12)	3.22	3.26
C(2)···C(15)	3.26	3.28
C(2)···C(12)	3.27	3.30
C(3)···C(13)	3.39	3.42

Table 4. *Least-squares planes*

The equation of each plane is in the form $l_1(SX) + l_2(SY) + l_3(SZ) + d = 0$, where SX , SY , SZ are orthogonal coordinates parallel to a , b and c^* . The atoms used to determine the plane are indicated by a boldface deviation from the plane.

Plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	
10^4l_1	4218	4657	4730	3933	9081	-9162	-7443	-9888	
10^4l_2	8214	7244	7250	7650	-4188	1739	6658	1334	
10^4l_3	3838	5084	5006	5100	6	3611	512	-665	
<i>d</i> (Å)	-1.607	-1.756	-1.733	-1.822	-1.328	-1.504	0.714	1.155	
Deviations (Å × 10 ³)									
C(1)	342		1050		-397	-1	-1	5	
C(2)	338		938						
C(3)	-561		-146						
C(4)	-227	-5	-24						
C(5)	-41	0	-22						
C(6)	177	5	-7						
C(7)	206	-7	-5						
C(8)	39	2	8	9					
C(9)	132	94	114	-5					
C(10)	-420	-228	-210	-415					
C(11)	-196	144	147	5	-372		-1	-5	
C(12)	1176		1602		8		-2		
C(13)	1423		2016		-8		2		
C(14)	-984		-288		8			-11	
C(15)	-1232		-706		-8			11	
C(16)	-173	3	-1	-9					
C(17)			1654				-6		
C(18)			1262				-4		
O(19)			758				7		
O(20)			2808				4		

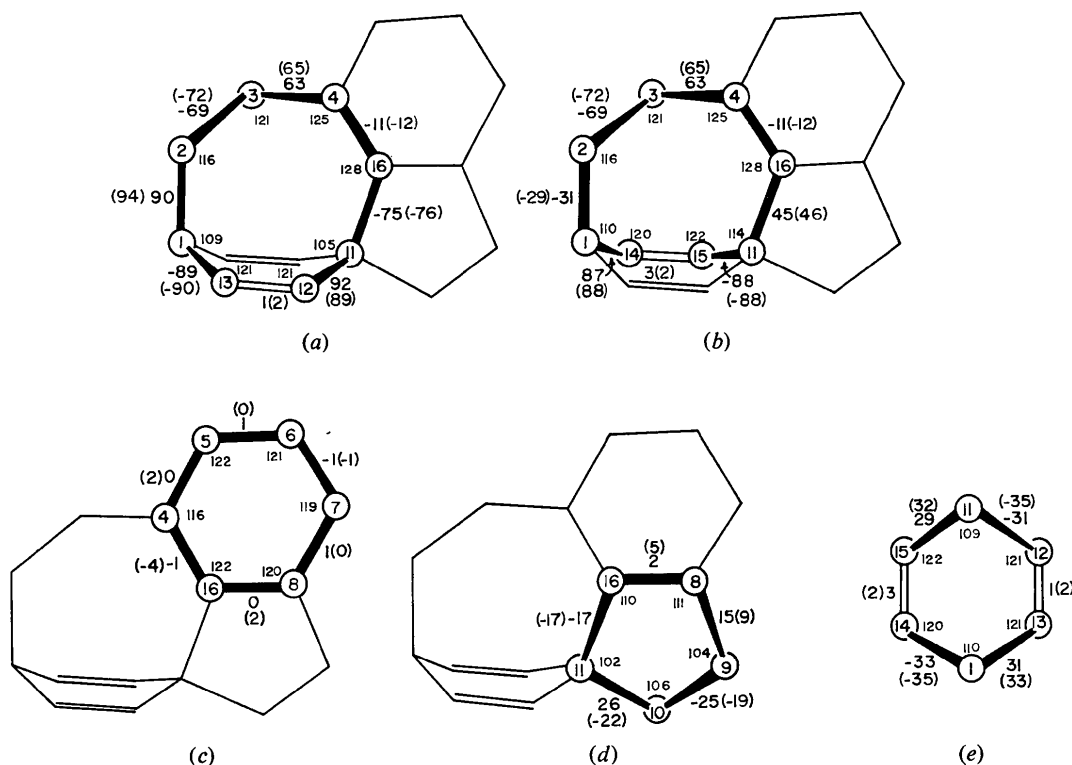


Fig. 6. Torsion and internal angles of the ring systems in (IV). Torsion angles in parentheses are the values calculated for the structure corresponding to minimum strain energy. All other values are calculated from the crystal structure parameters. (a) The eight-membered ring comprising carbon atoms 1, 2, 3, 4, 16, 11, 12, 13. (b) The eight-membered ring comprising carbon atoms 1, 2, 3, 4, 16, 11, 15, 14. (c) The aromatic ring. (d) The five-membered ring. (e) The cyclohexadiene ring.

Table 5. Short intermolecular distances

$H \cdots H$ distances less than or equal to 2.70 Å and $H \cdots C$, $H \cdots O$ distances less than or equal to 3.00 Å are included. The equivalent positions in the space group $P2_1/n$ are: I x, y, z ; II $-x, -y, -z$; III $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. Unit-cell translations are given in parentheses. Position I has the coordinates of Table 2.

	Position, cell translation	Distance (Å)	Vector (Fig. 7)
$H(10') \cdots H(13)$	IV(0, -1, 0)	2.30	<i>a</i>
$H(3) \cdots H(6)$	IV(-1, -1, 0)	2.52	<i>b</i>
$H(18') \cdots O(20)$	I(0, -1, 0)	2.58	<i>c</i>
$H(7) \cdots H(9)$	II(0, 1, 0)	2.65	<i>d</i>
$H(6) \cdots O(20)$	III(-1, 0, -1)	2.67	<i>e</i>
$H(2) \cdots H(2)$	II(0, 0, 1)	2.70	<i>e</i>
$H(9') \cdots H(15)$	I(0, 1, 0)	2.70	
$H(9) \cdots H(9)$	II(0, 0, 0)	2.70	
$H(15) \cdots C(8)$	I(0, 1, 0)	2.82	
$H(15) \cdots C(7)$	I(0, -1, 0)	2.90	
$H(18'') \cdots C(6)$	III(0, -1, 0)	2.92	
$H(3) \cdots O(20)$	II(0, 0, 1)	2.92	<i>f</i>
$H(2) \cdots O(20)$	II(0, 0, 1)	2.94	<i>h</i>

Table 3(c)], and near contacts of C(2) with O(19) and O(20), that minimize flexibility.

Some of the bond angles also differ from the values in strain-free structures, as a consequence of the constraints resulting from the presence of several ring systems. The agreement between the observed bond angles and those calculated by minimization of the strain energy [Table 3(b)] is remarkably good, in spite of the fact that angles at tetrahedral carbon atoms vary from 102 to 121° and those at trigonal carbon atoms from 110 to 128°.

Intermolecular heavy-atom distances are outside the range of normal van der Waals contacts; the shortest heavy-atom-heavy-atom distance is that from C(2) to O(20) [in the molecule at position II(0,0,1)], 3.51 Å. The packing is thus determined by the hydrogen atoms. Intermolecular distances (Fig. 7, Table 5) include two H-H contacts of less than 2.60 Å, and three H-C and four H-O contacts of less than 3.00 Å.

Ring geometry

The fused ring system of (IV) comprises two *cis* (formally) cyclooctadiene rings with six carbon atoms in common, a boat-shaped cyclohexadiene, and a benzene ring fused to a five-membered ring. Consideration of the ring conformations is complicated by the constraints imposed by the fused structure. Internal bond angles, shown in Fig. 6, are large in the region of the eight-membered ring that cannot readily relieve strain by twisting because it is fused to the planar aromatic ring; these angles are 126° at C(4) and 128° at C(16). The benzene ring is planar within experimental error (Table 4). The distances are normal, but the internal angle at C(4), 116°, reflects a small deformation of the ring, presumably due to the strain caused by fusion with the cyclooctadiene system.

The five-membered ring is puckered. Its shape can be described as an envelope, with the plane of the 'flap', C(9)-C(10)-C(11), making an angle of 27° with the plane of the envelope proper, C(11)-C(16)-C(8)-C(9). It has been noted (Cotton, Day, Frenz, Hardcastle & Troup, 1973) that the dihedral angle in non-planar cyclopentanes varies from 41° in free cyclopentane to 10° in a highly strained fused-ring structure, and that the dihedral angle bears a relationship to the internal angles in the ring. In particular, if the two adjacent internal angles in the envelope [at C(8) and C(16) in the present structure] are forced to be large, the dihedral angle between flap and envelope is small, and *vice versa*. The mathematical relationship between the dihedral angle and the internal angles (Dunitz, 1968; Dunitz & Waser, 1972), and the relatively stiff potentials for bond-stretching and bond-bending as compared with torsional strain, compel the ring to flatten to keep the remaining internal bond angles from becoming too small.

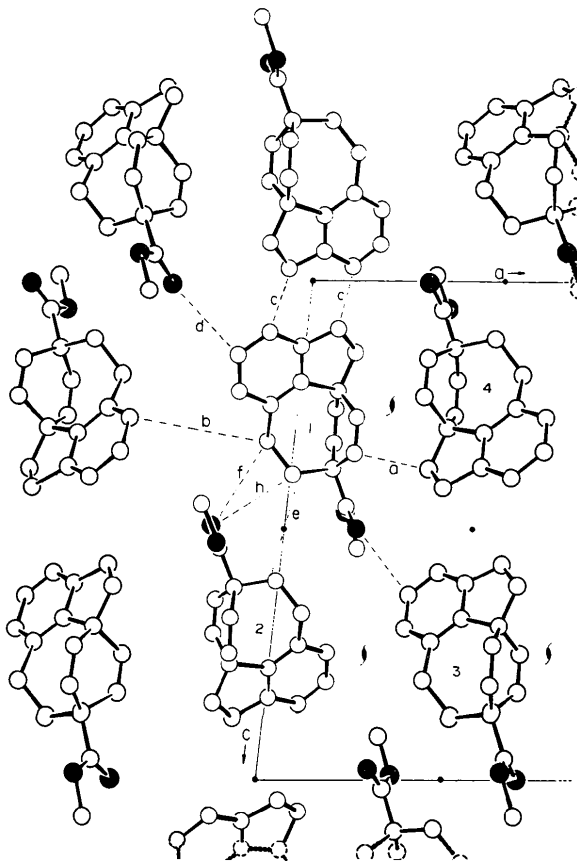


Fig. 7. The environment of the molecule in the crystal: perspective view of a portion of the unit cell of (IV) down the *b* axis. The viewing distance is about 80 Å. The intermolecular vectors shown are identified in Table 5; hydrogen atoms have, however, been omitted from the drawing. Molecules 1, 2, 3, 4 refer to positions I, II, III, IV (Table 5), with appropriate translations.

Considered alone, the cyclohexadiene 'boat' very nearly possesses *mm* symmetry (Figs. 2 and 6). C(1) and C(11) are 0.40 and 0.37 Å away from the plane of the olefinic carbon atoms (plane *E*, Table 4); the bond distances are symmetrical across a mirror plane through the double bonds, within two standard deviations. The asymmetry of the single-bond lengths across the perpendicular plane [through C(1) and C(11)] is just on the border of significance, three to five standard deviations. This asymmetry, as well as the larger torsion angle about C(14)–C(15) and the asymmetry of the internal angles at C(14) and C(15), may be due to the close contacts of this side of the ring with C(2) and C(3). No corresponding crowding is present on the C(12)–C(13) side of the ring.

If it is postulated that the two enantiomers present in the crystal represent positions near the two extremes of an oscillatory motion in solution, the crystal structure is entirely consistent with the results of the nuclear magnetic resonance study. The effects of such a motion are shown in Fig. 5; the 'bridge' atom, C(3), and the benzene ring would move through distances of about 1.4 Å, and the five-membered ring would invert. Other crystals known to contain enantiomeric pairs that appear to interchange rapidly (on the n.m.r. time scale) in solution at room temperature are those of the organometallic complexes $(C_8H_8)Ru_2(CO)_6$, $(C_8H_{10})Fe_2(CO)_6$, and $(C_{10}H_{12})Fe_2(CO)_6$ (Cotton & Edwards, 1968, 1969; Cotton & Frenz, 1972). In the present structure, it seems apparent that the enantiomeric pairs pack together efficiently; for example, the

close approach distances *a*, *b*, and *c* (Fig. 7 and Table 5) are attained by 'fitting together' the two opposite configurations.

Strain-energy calculations

The experimental parameters for this molecule – not only the details of the molecular geometry but also the barrier height for the internal motion that 'averages' the structures of the two enantiomeric conformers, as determined from low-temperature n.m.r. studies – invite comparison with values calculated by strain-energy minimization. The method used was that of Wiberg & Boyd (1972).

An approximate structure for the hydrocarbon skeleton of the molecule (V), deduced from a model, was used as a starting set of parameters for Boyd's program *MOLBD2* (Boyd, 1972). The structure reached by the program by means of iterative minimization of excess strain energy resembles the experimental results of the crystal study very closely; see Tables 3 and 4 and Fig. 6 for comparison. Potential functions and constants used in the calculations are summarized in Table 6. The excess strain energy of this structure is 24.1 kcal mol⁻¹; the barrier height for conversion to its mirror image through an intermediate with a plane of symmetry perpendicular to the cyclohexadiene ring was approximated by 'driving' the torsion angle C(1)–C(2)–C(3)–C(4) through 0°, while minimizing at each artificially maintained value of the torsion angle the other forms of intramolecular strain. The results are shown graphically in Fig. 8. The major portion of the barrier height is due to bond-angle strain, with torsional strain playing a minor role; in contrast, the strain energy attributed to bond stretching, out-of-plane bending and non-bonded interactions is almost constant over the entire proposed inversion path.

The barrier height, or difference between the excess strain energy at the top of the barrier and that of the minimum-energy conformation, is 11.5 kcal mol⁻¹. This figure is in good agreement with the experimental value of 9.2 ± 0.2 kcal mol⁻¹, inasmuch as the force constants used in the calculations were those derived from relatively strain-free molecules, and the molecule used in the experimental work contained the carbo-methoxy group at C(1) in place of the hydrogen atom used in the calculations.

The fact that the calculated barrier height is larger than the experimental value suggests some possible explanations for the discrepancy. It has been noted (Engler, Andose & Schleyer, 1973) that Boyd's potential functions tend to give a large value for angular strain, and the very large values for the internal angles at C(2), C(3), C(4) and C(16) of 122, 130, 132 and 130° respectively contribute a major portion of the strain energy in the proposed transition state. Also, it is possible though unlikely that the transition state model with the torsion angle C(1)–C(2)–C(3)–C(4) equal to zero does not represent the lowest energy inversion path.

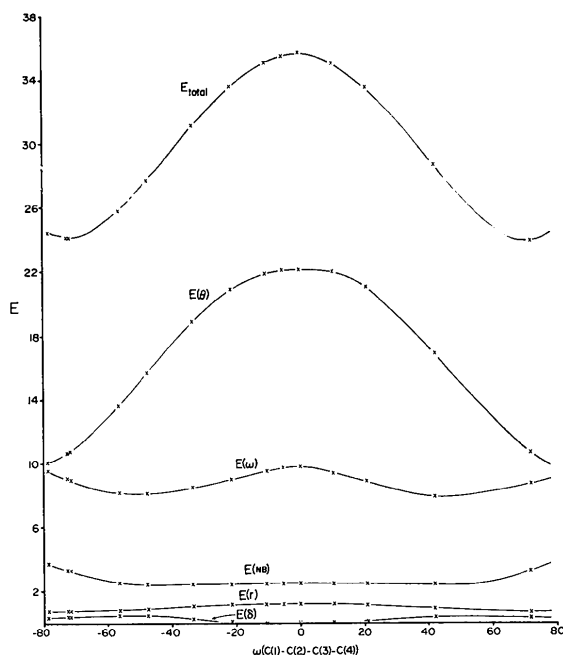


Fig. 8. Strain energy as a function of the torsion angle C(1)–C(2)–C(3)–C(4). For definition of the potential functions see Table 6. The torsion angle 0° corresponds to the conformation at the top of the ring-inversion barrier.

Table 6. *Parameters of strain-energy potential functions*

Functions and constants: Boyd (1972, 1973). The following symbols are used: C_a=aromatic sp² carbon; C_o=olefinic sp² carbon; C_t=tetrahedral carbon; C_x=C_o or C_t.

$$SE = E(r) + E(\theta) + E(\omega) + E(NB) + E(\delta).$$

(a) Bond stretching

	$k(\text{mdyn } \text{Å}^{-1})$	$r_0(\text{Å})$
C _a -C _a	7.65	1.390
C _a -C _t	4.40	1.500
C _t -C _t	4.40	1.530
C _t -C _o	5.10	1.500
C _o -C _o	6.85	1.335
C _a -H	5.05	1.090
C _t -H	4.55	1.090
C _o -H	5.08	1.090

(b) Bond bending

	$k(10^{-11}\text{ergs/molecule})$	$\theta_0(^{\circ})$
C _a -C _a -C _a	1.000	120.00
C _a -C _a -H	0.500	120.00
C _a -C _a -C _t	0.700	120.00
C _t -C _t -C _t	0.800	111.05
C _t -C _t -H	0.608	109.50
C _t -C _t -C _o	0.620	124.60
C _t -C _o -H	0.350	119.50
C _o -C _o -H	0.605	120.50
H-C _t -H	0.508	107.90

(c) Torsion

	$k(10^{-11}\text{ergs/molecule})$	$\omega_0(^{\circ})^*$
C _a -C _a -C _t -C _t	0.0010	60*
C _t -C _t -C _t -C _t	0.0146	60

	$k(10^{-11}\text{ergs/molecule})$	
C _a -C _a -C _a -C _a	-0.0800	0
C _t -C _o -C _o -C _t	-0.0785	0
C _t -C _t -C _o -C _o	0.0133	0

(d) Non-bonded

	A	B	C
C _x ···C _x	104.0	3.09	4.45
C _x ···C _a			
C _x ···H	30.0	3.415	0.960
C _a ···H			
H···H	18.4	3.740	0.190
C _a ···C _a †	0	0	0

(e) Out-of-plane bending‡

	$k(10^{-11}\text{ergs/molecule})$
C _a -C _a -C _a , C _t	0.800
C _a -C _a -C _a , H	0.290
C _o -C _o -H, C _t	0.210
C _t -C _o -C _o , H	0.135

* The strain energy due to torsion about bonds adjacent to the aromatic ring varied from 0.26 to 0.42 kcal mol⁻¹ for angles between -65 and 65°. Since the three terms in question are not important in the minimization, the energy is adequately represented by the threefold potential, at least over the range of angles in this calculation.

† The only type of C_a···C_a non-bonded interaction (1···4 across the aromatic ring) is considered to be included in the bond bending, torsion and out-of-plane bending potentials.

‡ δ is the complement of the angle between the normal to the plane defined by atoms I, J, K , and the vector $\overrightarrow{J-M}$.

Analysis of rigid-body motion

Since one would expect the highly strained fused-ring system in (IV) to be comparatively rigid, the temperature factors of the 16-carbon-atom skeleton were used in an analysis of the rigid-body motion of the molecule, with the results shown in Table 7 (Schomaker & Trueblood, 1968). The librational tensor, L , shows one principal axis of libration whose root-mean-square amplitude (5.1°) is significantly larger than those of the other two principal axes, and which is approximately parallel to (making an angle of 6.8° with) the axis of minimum inertia of the ring system. The root-mean-square deviation between the U_{ij} values derived from the experimental data and those derived from an assumption of rigid-body motion (ΔU_{ij}) was 0.0016 Å². Since this value is not significantly larger than the r.m.s. standard deviation for the observed U_{ij} values themselves (average e.s.d. about 0.0015 Å², average U_{ij} about 0.05 Å²), and since this e.s.d. is quite low, the rigid-body parameters seem to give a meaningful representation of the thermal motion of the molecule.

Table 7. *Rigid-body motion parameters*

Notation of Schomaker & Trueblood (1968). The values of T and S are relative to the centroid of the skeleton. E.s.d.'s appear in parentheses. Reference axes are a, b, c^* .

Centroid of the 16-atom skeleton: 0.0245, 0.0454, 0.2266 in crystal coordinates.

$L \times 10$ (deg ²)	78 (5)	-30 (3)	74 (3)
		109 (4)	-67 (4)
$T \times 10^4$ (Å ²)	444 (6)	7 (5)	185 (6)
		457 (7)	-43 (5)
$S \times 10^4$ (rad Å)	-1 (3)	1 (1)	509 (5)
	-31 (1)	-1 (3)	2 (2)
	15 (2)	-36 (1)	5 (1)

Principal axes	Value	Direction cosines		
L	26.0 deg ²	-401	446	-800
	7.4	-285	-893	-348
	4.0	-872	85	483
T^*	0.0556 Å ²	-397	-306	866
	0.0414	382	-914	-143
	0.0386	837	272	475
S^*	0.1370 deg Å	192	-476	859
	-0.0401	973	0	-234
	-0.0973	115	866	485

$$\sqrt{\sum(\Delta U_{ij})^2/(m-s)} = 0.0016 \text{ Å}^2$$

Axes of minimum inertia

	Direction cosines		
16-atom skeleton	-384	546	-745
20-atom molecule	-286	468	-836

* Principal axes of T and S are transformed to the principal axes of L (reduced T and S , after symmetrizing S). Direction cosines refer to the original orthogonal axes a, b, c^* .

Corrections to bond lengths made with rigid-body parameters (Table 3) are at the border of significance, of the order of one or two standard deviations. The

ΔU_{ij} values for C(3), C(4), C(5), C(6) and C(7) (which are presumed to be oscillating rapidly in solution) are not significantly larger than those for the other atoms; they apparently have in the crystal little additional thermal motion beyond that corresponding to movement of the molecular skeleton as a whole, in keeping with the relatively high barrier height.

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