

in the usual manner. Sets of five different solutions were irradiated in parallel with the peroxide being studied. After irradiation, the contents of the ampoules were washed into 50-ml volumetric flasks, diluted with absolute methanol, and allowed to stand for 12–24 hr. The concentration of benzophenone before and after irradiation was then determined by measuring the uv absorption at 333 nm on a Beckman Model DU spectrophotometer. Originally the uv absorption was determined at several wavelengths as described by Hammond and Foss but this practice was abandoned when it was found that the average absorption was invariably very close to the reading at 333 nm. Apparently dilution with methanol instead of benzene solved whatever problem Hammond and Foss encountered.

Ferrioxalate Actinometry. The procedures of Hatchard and Parker^{19a} and Calvert and Pitts³ were used. The ferrioxalate concentration was set at 0.15 M to ensure that all light would be absorbed in the 16-mm tubes used. The best determination of the quantum yield for ferrous ion production upon irradiation of this concentration of potassium ferrioxalate with 366-nm light was made by Lee and Seliger who found Φ to be 1.20.^{19b} An inert atmosphere was not used in the ferrioxalate actinometric experiments because of statements in the literature that it is not necessary.^{3,19a} We found, however, that our ferrioxalate quantum yields were consistently higher than those obtained with the other actinometers.

Benzophenone-Piperylene Actinometry and Triplet Counting. A 4-ml aliquot of a 2 M stock solution of *trans*-piperylene in specially purified benzene⁴⁵ was added to 0.6 g of zone-refined benzophenone and diluted to 50 ml in a volumetric flask. For *m*-BBP triplet counting a 25-ml volumetric flask containing 0.4725 g of *m*-BBP was given a 2-ml aliquot of the stock piperylene. Five-milliliter aliquots of these solutions were degassed as usual, with liquid nitrogen as the coolant to prevent loss of piperylene. Glc analysis of the solutions before analysis showed that the solution contained 1.34% cyclopentene, 98.10% *trans*-piperylene, and 0.55% *cis*-piperylene. The concentration of piperylene corrected for cyclopentene was 0.1585 M. After irradiation both the benzophenone-piperylene solution and the *m*-BBP-piperylene solution

(45) Benzene purified by selective photochemical chlorination of the hydrocarbon impurities was supplied by L. Metts and J. Saltiel.

were found to contain 2.52% *cis* based upon the area of the piperylene peaks.

Product Studies. The products from the thermal decomposition and photolyses of the peroxides were determined by conventional gas-liquid chromatographic methods.⁶ The glc peaks were identified by collecting them on the plates of a Wilks Scientific Co. MIR-15 GC-IR multiple internal reflectance infrared cell.

For the internal competition experiment with *m,p'*-DP, that peroxide was irradiated until 30.4% of the original titer was lost. Chlorobenzene and hexachloroethane were determined in the usual way from one aliquot. The other products were determined from another aliquot after reduction of the remaining peroxides to the carboxylic acids with NaI in acetone. The acids were converted to their methyl esters by means of diazomethane; then the mixture was analyzed by glc for *m,p'*-dichlorobenzophenone, carbomethoxy-chlorobenzophenones, and *m,p'*-dicarbomethoxybenzophenone. Since the peak containing the *m*-carbomethoxy-*p'*-chlorobenzophenone and the *p*-carbomethoxy-*m'*-chlorobenzophenone could not be resolved, the mixture of these two esters was analyzed by means of its infrared spectrum, using the computer program ANALYZ.⁴⁶

Synthesis of the Peroxides. Standard safety precautions included the use of all-glass equipment (including spatulas), explosion shields, and restriction of the experiments to a small scale. Of the new peroxides, only benzoyl *m*-{*p*-[(benzoyldioxy)carbonyl]benzoyl}benzoyl peroxide could be detonated with a hammer and it seemed to be less sensitive to shock than α -naphthoyl peroxide. The unsymmetrical peroxides were prepared by the technique of Greene and Kazan⁴⁷ from the corresponding acids, perbenzoic acid, and dicyclohexylcarbodiimide. Melting points, infrared spectra, and analyses of all of the peroxides are recorded in Table VII.

Acknowledgment. The authors wish to thank Professor J. Saltiel and his collaborators for many helpful discussions. Financial support of this research by the Chemistry Programs, National Science Foundation Grants No. GP 8015 and GP 15991, is gratefully acknowledged.

(46) D. F. DeTar, *Anal. Chem.*, **38**, 1794 (1966).

(47) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

Crystal and Molecular Structure of the Photodimer of 5,6,7,8-Tetrahydro-2-quinolone

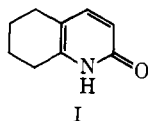
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Received March 8, 1971

Abstract: The crystal and molecular structure of 1,3,4,7,8,9,10,11-octahydro-2*H*,5*H*-4a,11:10a,5-bis(iminomethano)dibenzo[*a,e*]cyclooctene-13,16-dione has been determined by a single-crystal X-ray diffraction study using diffractometer data. The compound crystallizes in the space group $P2_1/c$ with $a = 9.892(1) \text{ \AA}$, $b = 10.431(1) \text{ \AA}$, $c = 7.272(1) \text{ \AA}$, $\beta = 107.75(1)^\circ$, $Z = 2$. The structure was determined by the symbolic addition method and refined by block-diagonal least squares to a final R value of 0.047 for the 1064 statistically significant, independent reflections. The C-C bond distance between monomer moieties, 1.623 (0.003) \AA , is significantly longer than a normal C-C single bond and the amide system exhibits substantial conjugation.

Reactions involving the photolysis of 5,6,7,8-tetrahydro-2-quinolone (I) at 3500 \AA yielded a highly labile and extremely insoluble compound. Its ir spec-



trum (Nujol) showed an unconjugated lactam absorp-

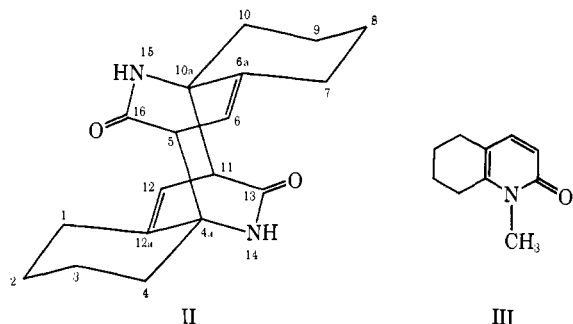
tion at 1660 cm^{-1} . Because of the extreme insolubility of the compound in the common organic solvents, no detailed ir, uv, or nmr spectra could be obtained. Mass spectral studies gave a molecular ion at m/e 149 which was identical with that obtained for I. Similarly, an nmr spectrum in trifluoroacetic acid was identical in every respect with that of the parent compound. The new compound must, therefore, be highly labile and readily revert to the starting material.¹

Table I. Final Least-Squares Parameters (Esd Refers to Last Digit; $\beta \times 10^4$)^a

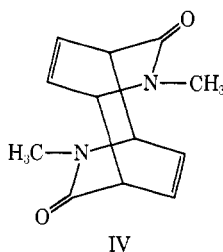
Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	0.1516 (2)	0.0226 (2)	0.1615 (3)	56 (3)	51 (3)	60 (5)	-5 (2)	19 (3)	-6 (3)
C2	0.2906 (3)	0.0754 (3)	0.2986 (3)	69 (3)	75 (3)	76 (5)	-8 (3)	12 (3)	-15 (4)
C3	0.4175 (3)	0.0489 (3)	0.2278 (4)	76 (4)	103 (4)	110 (6)	-17 (3)	25 (4)	-3 (4)
C4	0.4360 (3)	-0.0942 (3)	0.2075 (4)	65 (4)	111 (4)	131 (7)	17 (3)	24 (4)	6 (4)
C5	0.3074 (3)	-0.1478 (3)	0.0550 (4)	83 (4)	83 (4)	115 (6)	19 (3)	31 (4)	-9 (4)
C6	0.1675 (3)	-0.1093 (2)	0.0803 (3)	68 (3)	48 (3)	60 (5)	6 (2)	17 (3)	-1 (3)
C7	0.0509 (3)	-0.1782 (2)	0.0181 (3)	92 (4)	36 (3)	82 (5)	6 (3)	23 (4)	-3 (3)
C8	-0.0896 (3)	-0.1215 (2)	0.0166 (3)	80 (3)	40 (3)	69 (5)	-12 (2)	22 (3)	-4 (3)
C9	-0.0679 (3)	-0.0574 (2)	0.2110 (3)	82 (4)	48 (3)	55 (5)	3 (3)	26 (3)	15 (3)
N	0.0524 (2)	0.0095 (2)	0.2749 (3)	66 (3)	58 (2)	48 (4)	-10 (2)	22 (3)	-12 (3)
O	-0.1509 (2)	-0.0719 (2)	0.3058 (2)	87 (3)	89 (2)	78 (4)	-6 (2)	40 (2)	10 (3)

^a Anisotropic temperature factors of the form $e^{-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl}$ were used.

Based primarily on the negative results above, a dimeric structure was postulated for this new compound (II). Attempts were then made to prepare the *N*-methyl analog of the dimer starting from III. All



such attempts proved fruitless.² The dimeric system IV, which is somewhat analogous, has been shown by a previous X-ray structure to have "intermonomer" bonds of 1.6 Å,³ and to be very labile.



The lability of the compound prepared from I, the decomposition back to I, the lack of success in making the *N*-methyl analog, and the aforementioned long intermonomer bond in a simpler system thus suggest the following hypotheses: (a) a dimer is also formed in this instance; (b) this dimer has very long intermonomer bonds; (c) attempts to make substituted analogs failed because they would require this very long intermonomer bond to be beyond the critical distance necessary for bonding to occur. For these reasons, a single-crystal, X-ray study of the product formed during the photolysis of I was undertaken.

Experimental Section

A sample of this compound was kindly supplied to us by Professor A. I. Meyers.⁴ One of the crystals ($0.12 \times 0.15 \times 0.15$ mm)

- (1) A. I. Meyers and P. Singh, *J. Org. Chem.*, **35**, 3022 (1970).
- (2) P. Singh, Ph.D. Thesis, Louisiana State University in New Orleans, Oct 31, 1968.
- (3) M. Laing, *Proc. Chem. Soc., London*, 343 (1964).
- (4) A. I. Meyers, private communication (and sample), June 1970.

from this sample was used for the cell constant and symmetry determination and the collection of data.

The crystal was mounted with the (0*kl*) axis parallel to the ϕ axis of the goniometer of a General Electric XRD-5 diffractometer and the symmetry and cell constants were determined using Cu K α radiation. Extinctions for the (0*kl*) line when $k = 2n + 1$ and in the (*h*0) plane when $l = 2n + 1$ led unambiguously to the monoclinic space group, $P2_1/c$ —no. 14. Cell constants were then calculated from the least-squares refinement of 28 reflections with 2θ values greater than 78° allowing independent measurements of the K α_1 and K α_2 doublet for copper. The results with their estimated standard deviations (esd's) are: $a = 9.892 \pm 0.001$ Å; $b = 10.431 \pm 0.001$ Å; $c = 7.272 \pm 0.001$ Å; $\beta = 107.75 \pm 0.01^\circ$. The experimental density of 1.41 ± 0.05 g/cm³, measured by a flotation method, agrees well with the density of 1.386 g/cm³ calculated by assuming two dimer molecules per unit cell.

Three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer system using the stationary crystal-stationary counter method, balanced nickel-cobalt filters, and copper radiation to the limit, $2\theta = 140^\circ$ ($d = 0.820$ Å). Of the 1438 independent reflections measured, 1064 (74%) were considered observed by the criteria $(I_{Ni} - 2\sigma_{Ni}) - (I_{Co} + 2\sigma_{Co}) > 50$ counts, 10-sec counting time.

A correction for $\alpha_1 - \alpha_2$ splitting was made but no absorption correction seemed necessary (linear $\mu = 7.35$ cm⁻¹ and no more than 2% difference in a ϕ scan at $\chi = 90^\circ$). Lorentz-polarization corrections were made and the intensities were reduced to structure amplitudes in the usual manner; σ 's in the structure amplitudes were based on counting statistics.

Structure Determination.⁵ Normalized structure magnitudes $|E|$'s were calculated using a K curve, as described by Karle and Hauptman.⁶ Phases of 247 E 's (from a total of 274 with $E > 1.5$) were determined by the symbolic addition procedure^{7a} in terms of one symbolic sign a , no phase being accepted below a probability of 0.999. E maps were calculated corresponding to both signs of a . The first map contained two reasonable six-membered rings but would not refine below $R = 0.50$, whereas, the second map contained only eleven peaks, approximately equal in height, corresponding to the coordinates of the nonhydrogen atoms in the expected structure with the dimer inversion center at $(0, 0, 1/2)$. Several cycles of block-diagonal, least-squares refinement of the coordinates and isotropic temperature factors of the eleven nonhydrogen atoms using unit weights led to a value of $R = 0.15$. This was followed by conversion of the isotropic temperature factors to anisotropic temperature factors and several more cycles of similar refinement which gave an R value = 0.10.^{7b}

A difference electron density map, phased by the nonhydrogen atoms, was calculated. Distinct peaks (approximately 0.5 e/Å³) were found for hydrogen atoms bonding to carbon atoms. Since

(5) Structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(6) J. Karle, H. Hauptman, and C. L. Christ, *Acta Crystallogr.*, **11**, 757 (1958).

(7) (a) The symbolic addition procedure was computed *via* the program DIRECT written in Fortran IV by J. N. Brown for the P.D.P.-10 computer (1969). (b) Scattering factors were taken from: D. Cromer and J. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

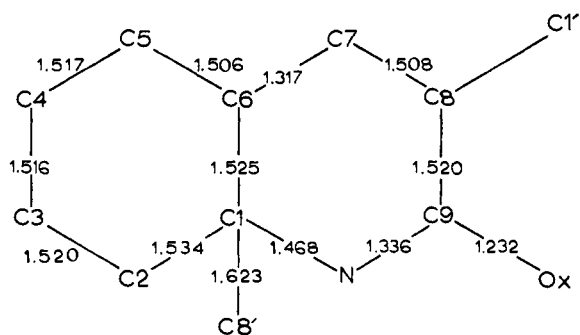


Figure 1.

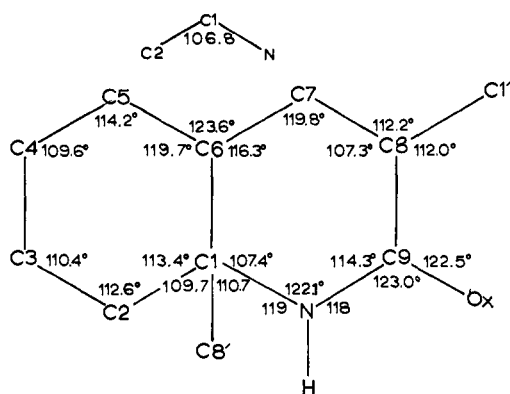


Figure 2.

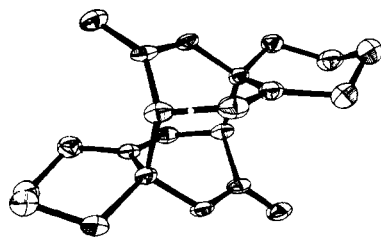


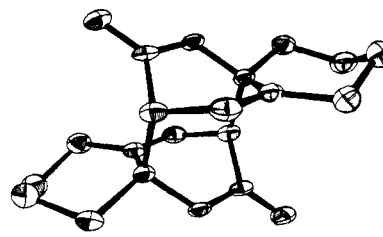
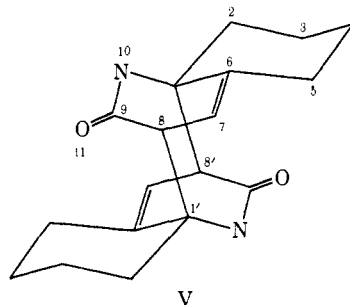
Figure 3.

Table II. Refined Hydrogen Coordinates and Isotropic Temperature Factors (Atom Numbers Refer to Bonding Atom—Esd Refers to Last Digit)

Atom	X	Y	Z	β_{isot}
H2	0.274 (2)	0.172 (2)	0.323 (3)	2.6 (6)
H2'	0.313 (2)	0.003 (2)	0.429 (3)	2.0 (6)
H3	0.403 (2)	0.096 (2)	0.094 (3)	3.4 (7)
H3'	0.498 (2)	0.096 (2)	0.328 (3)	3.4 (7)
H4	0.521 (3)	-0.120 (3)	0.175 (4)	5.2 (8)
H4'	0.452 (2)	-0.140 (2)	0.339 (3)	2.6 (6)
H5	0.304 (2)	-0.116 (3)	-0.072 (3)	3.0 (6)
H5'	0.312 (3)	-0.244 (3)	0.050 (3)	3.2 (6)
H7	0.050 (2)	-0.260 (2)	-0.031 (3)	3.4 (7)
H8	-0.162 (2)	-0.188 (2)	0.002 (3)	2.8 (6)
HN	0.078 (2)	0.037 (2)	0.393 (3)	2.1 (6)

Discussion

The compound has the structure (renumbered for convenience) shown below (V). The final coordinates and anisotropic temperature factors of the nonhydro-



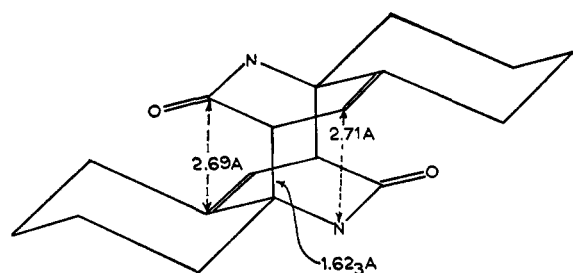
the nitrogen was expected to exhibit tetrahedral bonding symmetry, it was anticipated that the hydrogen bonded to it would occupy one of two available tetrahedral positions or be disordered between these two positions. Instead, the map showed a single distinct peak ($0.5 \text{ e}/\text{\AA}^3$) at 0.96 \AA from the nitrogen and forming 120° angles about the nitrogen. These eleven peaks accounted for all electron density greater than $0.25 \text{ e}/\text{\AA}^3$. Five more cycles of block-diagonal least squares, with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms, lowered the R value to 0.06. At this point, it was noticed that two reflections, (020) and (100), had structure factors calculated much higher than observed. Examination of the intensity data showed that these two reflections and the $(\bar{1}, 1, 1)$ were beyond the linearity limit of the detecting system and, therefore, all three reflections were omitted from further least-squares refinements.

The inversion center of the dimer was shifted to (0, 0, 0) for convenience and the least-squares refinement was restarted with isotropic temperature factors for all 22 atoms and with $1/\sigma^2$ weights. (This and all subsequent refinements varied coordinates and temperature factors of all atoms.) After ten cycles of least squares, the isotropic temperature factors of the nonhydrogen atoms were converted to anisotropic temperature factors. Ten additional cycles, led to convergence at a value of $R = 0.047$ with all shifts much less than 0.1 the estimated standard deviation of the respective variable. A new difference map showed no region greater than $0.2 \text{ e}/\text{\AA}^3$ and thus the structure determination was considered complete.

gen atoms, together with their estimated standard deviations, are given in Table I. The refined coordinates and isotropic temperature factors of the hydrogens are listed in Table II. The final distances and angles are illustrated in Figures 1 and 2 and an ORTEP stereo-diagram is given as Figure 3.

The molecule is a head-to-tail photodimer of 5,6,7,8-tetrahydro-2-quinolone with the monomer units bonded by carbon-carbon single bonds from C1-C8' and C1'-C8 (primes indicate centrosymmetric equivalents). The two six-membered pyridone rings, across which dimerization occurs, are in the boat form minimizing the steric interaction between the rings.

The intermonomer bonds (C1-C8' and C8-C1') are $1.623 (3) \text{ \AA}$ in length and represent the longest such bonds found in the literature. These distances account very nicely for the high lability of the dimer in its facile reversal to the monomer. These bonds are about 0.08 \AA longer than the normal carbon-carbon single bond and significantly longer than the equivalent bonds in similar compounds. Perhaps the best comparison is to the intermonomer bonds in 1-methyl-2-pyridone³



TRANSANNULAR CLOSE CONTACTS

Figure 4.

(IV). The slightly longer bonds in our study are most easily accounted for by the added bulk of the fused six-membered ring. Other long carbon-carbon bonds (1.58–1.60 Å) have been observed in photodimers of cyclopentanone,⁸ 1,3-dimethylthymine,⁹ benzocyclobutadiene,¹⁰ and thymine.¹¹ In these cases, however, these long bonds are found in highly strained cyclobutadiene rings which were formed in the dimerization process.

This system, on the other hand, is highly strained because the monomer units are bound together in such a way that short contact distances between these units exist. These short distances of 2.69 Å for C9–C6' and 2.71 Å for N–C7' are illustrated in Figure 4. Short contact distances analogous to these were also observed in the aforementioned determination of the structure of the 1-methyl-2-pyridone photodimer.

A surprising feature is the shortened N–C9 bond (1.336 Å) and near sp^2 hybridization of the nitrogen atom indicative of significant delocalization along the N–C9–O bonds. Supporting this hypothesis are the H–N–C angles (119, 118°) and the CNC angle of 122.1°. Finally, this delocalization and rehybridization is further supported by the planarity of the ring atoms N, C1, C8, C9, and the oxygen. The least-squares best plane (equation: $-0.3745P + 0.8131Q - 0.4457R = -0.731$) has a standard deviation of 0.01 Å with C9 at the greatest distance (0.02 Å) from this plane. The short N–C9 distance (1.336 Å) is between that observed in 3-methyl-2-pyridone (1.36 Å) and the standard carbon-nitrogen double bond distance of 1.302 Å.¹²

The pyridone rings in the dimer are in the boat form with dihedral angles of 141.5 and 144.2°. The fused cyclohexane rings are in the chair conformation as

(8) T. N. Margulis, *Acta Crystallogr.*, **18**, 742 (1965).

(9) N. Camerman, D. Weinblum, and S. C. Nyburg, *J. Amer. Chem. Soc.*, **91**, 982 (1969).

(10) B. L. Barnett and R. E. Davis, *Acta Crystallogr., Sect. B*, **26**, 1026 (1970).

(11) N. Camerman and S. C. Nyburg, *ibid.*, *Sect. B*, 388 (1969).

(12) L. M. Trefonas, R. L. Flurry, Jr., R. Majeste, E. A. Meyers, and R. F. Copeland, *J. Amer. Chem. Soc.*, **88** 2145 (1966).

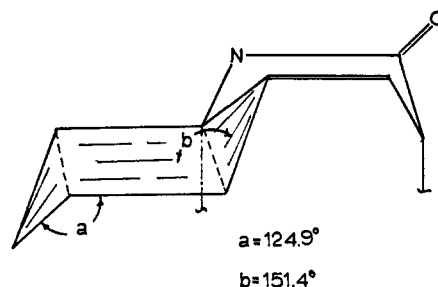
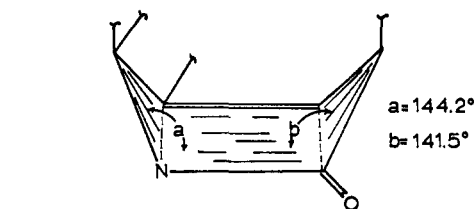


Figure 5.

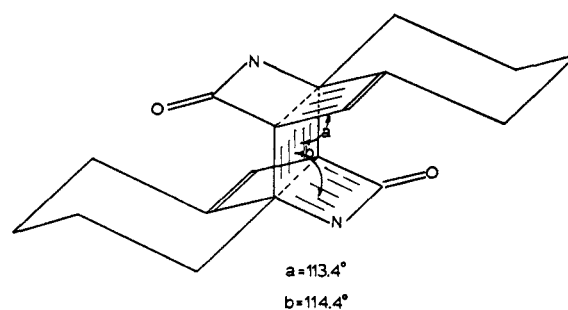


Figure 6.

expected, although the dihedral angle near the ring fusion (151.4°) is appreciably greater than that of the other dihedral angle (124.9°) which is quite near the theoretical value of 120°. The rehybridization of C6 is the apparent cause of this flattening. These planes and dihedral angles are illustrated in Figure 5. The dihedral angles at the fusion points of the monomer units (within the eight-membered ring) are 114.4° and 113.4°, lower than would be expected in a normal ring system (Figure 6). Hence, these support the previously postulated high degree of strain in the central portion of the dimer molecule. The inability to dimerize the *N*-methyl-2-quinolone derivative is readily attributed to the strained nature of this part of the system, the close contacts already existent, and the added bulk of the *N*-methyl group over that of hydrogen.

The dimer molecules are bound by hydrogen bonding along the *z* axis of the unit cell. The nitrogen of one monomer is linked to the oxygen of the centrosymmetrically related monomer unit translated by one unit cell length.