

Crystal structure and molecular conformation of 2,3-dicyclopropyl-1,4-naphthoquinone

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Crystals of the title compound are orthorhombic with $a = 8.483(4)$, $b = 18.249(9)$, $c = 15.889(8)$ Å, space group $Pbca$, $Z = 8$. The quinone ring shows distinct distortions from planarity. The solution n.m.r. spectra of the compound at various temperatures suggest a measure of restricted rotation about the cyclopropyl-quinonoid bonds. This is partially substantiated by a conformational analysis using the method of atom pair potentials.

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Kristalle van die titelverbinding is ortorombies met $a = 8.483(4)$, $b = 18.249(9)$, $c = 15.889(8)$ Å, ruimtegroep $Pbca$, $Z = 8$. Die kinoonring toon duidelike afwykings van planêriteit. Die k.m.r.-spektra van die verbinding in oplossing by verskillende temperature dui op 'n mate van beperkte rotasie om die siklopropiel-kinonoïedbindings. Dit word gedeeltelik bevestig deur 'n konformasie-analise volgens die metode van atoompaar-potensiale.

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Molecules satisfying the so-called Hückel (or $4n + 2$) rule are well known to have an unusually high stability.¹ Thus, the aromaticity of the cyclopentadienide anion has been ascribed to its possessing six π -electrons ($n = 1$). The synthesis of benz[*f*]indene-4,9-quinone was attempted with a view to studying the chemistry of its anion, which is iso-electronic with anthraquinone. A possible route to the isolation of this compound necessitated the formation of 2-cyclopropyl-1,4-naphthoquinone as a substrate.² An early fraction in the chromatographed products of this reaction yielded 2,3-dicyclopropyl-1,4-naphthoquinone as a by-product in the form of yellow crystals. The interesting nature of the ¹H n.m.r. spectrum at room temperature of this by-product, which exhibited a highly symmetrical pattern about the methylene and methine proton absorption region, prompted further investigations into its structure and conformation.

The compound was prepared as detailed by Giles *et al.*²

Experimental

Crystallographic analysis

Preliminary oscillation and Weissenberg photographs, taken about the three principal axes, gave the space group $Pbca$. The cell parameters were obtained from a least-squares analysis of the settings of 25 reflections measured on a four-circle PW1100 diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.7107$ Å). During the diffractometer data collection, three reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details of the data collection are listed in Table 1. The data were corrected by a Lorentz-polarization factor, but not for absorption.

The structure was solved by the automatic centrosymmetric routine of the SHELX program system,³ in which an E map yielded the positions of all the heavy atoms. Subsequent least-squares refinement, with all atoms treated isotropically, yielded the positions of most hydrogen atoms and these were then included in the model by the technique of constrained refinement, with $d(C-H) = 1.08$ Å and their positions dictated by the geometry of the molecule. Because of the unusual geometry at C(21) and C(31), the methine hydrogen atoms cannot be placed by this method. We therefore omitted the methine hydrogen atoms from a structure factor calculation, found their positions in a difference electron density map, and finally allowed all hydrogen atoms in the cyclopropyl rings to refine with a simple bond-length constraint of 1.08 Å from their parent atoms. The final geometry of the cyclopropyl moieties compared favourably with that previously found in *N,N*-dimethyl-2-phenylcyclopropylamine hydrochloride⁴ and α -cyano-3-phenoxybenzyl-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate,⁵ in which no constraints had been applied to the hydrogen atoms. The isotropic temperature factors of all

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the hydrogen atoms were treated as three single parameters, whose final values are reported in Table 1. Final atomic parameters, and principal bond lengths and angles are shown in Tables 2, 3, and 4 respectively. Figure 1 shows the molecule viewed perpendicularly to the two aromatic rings. A distinctive feature of the structure is the considerable distortion

Table 1 Crystal data and experimental and refinement parameters for the structure analysis

Crystal data	
Molecular formula	C ₁₆ H ₁₄ O ₂
<i>M_r</i>	238
Space group	Pbca
<i>a</i>	8,483(4) Å
<i>b</i>	18,249(9) Å
<i>c</i>	15,889(8) Å
<i>V</i>	2459,7 Å ³
<i>D_m</i>	1,27 g cm ⁻³
<i>D_c</i>	1,29 for <i>Z</i> = 8
<i>μ</i> (Mo-Kα)	0,47 cm ⁻¹
<i>F</i> (000)	1008
Data Collection	
Crystal dimensions	0,1 × 0,1 × 0,5 mm
Scan mode	ω -2 θ
Scan width	1,1° θ
Scan speed	0,03° θ s ⁻¹
Range scanned (2 θ)	6°—40°
Stability of standard reflections	0,84%
Number of reflections collected	1358
Number of 'observed' reflections	489 with <i>I</i> (rel) > 2 σ <i>I</i> (rel)
Final refinement	
Number of variables	106
$R = \Sigma F_o - F_c / \Sigma F_o $	0,096
$R_w = \Sigma w^2 F_o - F_c / \Sigma w^2 F_o $	0,071
Weighting scheme <i>w</i>	($\sigma^2 F$) ⁻¹
<i>U</i> (aromatic H)	0,167 Å ²
<i>U</i> (methine H)	0,112 Å ²
<i>U</i> (methylene H)	0,117 Å ²

Table 2(a) Fractional atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^3$) Å² of the heavy atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(1)	23(16)	3 167(7)	2 039(8)	46(4)
C(2)	29(14)	2 879(7)	2 922(8)	39(4)
C(21)	-668(16)	2 143(8)	3 074(8)	53(4)
C(22)	356(18)	1 574(9)	3 475(11)	75(5)
C(23)	18(19)	1 509(9)	2 554(11)	71(4)
C(3)	535(14)	3 315(7)	3 563(9)	41(4)
C(31)	276(18)	3 088(8)	4 433(9)	60(5)
C(32)	17(19)	3 629(8)	5 178(9)	65(5)
C(33)	1 531(20)	3 205(8)	5 133(10)	72(5)
C(4)	1 358(16)	4 024(8)	3 382(8)	56(5)
C(41)	1 624(15)	4 242(6)	2 474(9)	43(4)
C(5)	2 551(16)	4 845(7)	2 300(8)	56(4)
C(6)	2 717(17)	5 049(6)	1 451(8)	64(5)
C(7)	1 988(17)	4 649(7)	828(9)	70(5)
C(8)	1 076(18)	4 036(8)	983(9)	67(5)
C(81)	911(15)	3 829(7)	1 843(8)	42(4)
O(1)	-761(10)	2 841(5)	1 512(6)	70(3)
O(4)	1 854(10)	4 425(5)	3 930(6)	81(4)

Table 2(b) Fractional atomic coordinates of the hydrogen atoms ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
H(21)	-192	219	320
H(221)	-20	119	390
H(222)	159	168	358
H(231)	-114	132	235
H(232)	94	157	209
H(31)	-5	254	464
H(321)	-83	337	559
H(322)	-5	420	502
H(331)	150	272	553
H(332)	256	353	499
H(5)	309	516	280
H(6)	347	551	129
H(7)	210	484	19
H(8)	54	373	48

Table 3 Bond lengths (Å) with e.s.d.'s

Bond	Length	Bond	Length
O(1)-C(1)	1,223(13)	C(3)-C(4)	1,497(15)
C(1)-C(2)	1,498(12)	O(4)-C(4)	1,212(13)
C(2)-C(21)	1,488(16)	C(4)-C(41)	1,513(16)
C(21)-C(22)	1,495(19)	C(41)-C(5)	1,381(14)
C(21)-C(23)	1,536(19)	C(5)-C(6)	1,406(15)
C(22)-C(23)	1,496(21)	C(6)-C(7)	1,377(14)
C(2)-C(3)	1,362(14)	C(7)-C(8)	1,383(16)
C(3)-C(31)	1,460(17)	C(8)-C(81)	1,423(14)
C(31)-C(32)	1,556(19)	C(41)-C(81)	1,393(15)
C(31)-C(33)	1,554(19)	C(1)-C(81)	1,458(15)
C(32)-C(33)	1,501(20)		

Table 4 Selected bond angles (°) with e.s.d.'s

Bonds	Angle	Bonds	Angle
O(1)-C(1)-C(2)	118,2(1,3)	C(3)-C(31)-C(33)	122,4(1,3)
O(1)-C(1)-C(81)	122,5(1,3)	C(32)-C(31)-C(33)	57,7(0,9)
C(2)-C(1)-C(81)	119,3(1,2)	C(32)-C(31)-H(31)	108,7(6,4)
C(1)-C(2)-C(21)	117,9(1,2)	C(33)-C(31)-H(31)	94,8(6,7)
C(21)-C(2)-C(3)	122,1(1,3)	C(31)-C(32)-C(33)	61,1(1,0)
C(1)-C(2)-C(3)	119,8(1,2)	C(31)-C(33)-C(32)	61,2(1,0)
C(2)-C(21)-H(21)	110,4(6,2)	C(3)-C(4)-C(41)	118,6(1,2)
C(2)-C(21)-C(22)	117,7(1,2)	O(4)-C(4)-C(3)	123,1(1,3)
C(2)-C(21)-C(23)	116,2(1,3)	O(4)-C(4)-C(41)	118,3(1,3)
C(22)-C(21)-C(23)	59,1(0,9)	C(4)-C(41)-C(5)	119,0(1,4)
C(22)-C(21)-H(21)	123,0(6,3)	C(4)-C(41)-C(81)	118,7(1,2)
C(23)-C(21)-H(21)	122,0(6,1)	C(5)-C(41)-C(81)	122,2(1,4)
C(21)-C(22)-C(23)	61,8(1,0)	C(41)-C(5)-C(6)	117,4(1,3)
C(21)-C(23)-C(22)	59,1(1,0)	C(5)-C(6)-C(7)	120,3(1,3)
C(2)-C(3)-C(4)	120,5(1,3)	C(6)-C(7)-C(8)	123,5(1,4)
C(2)-C(3)-C(31)	119,7(1,3)	C(7)-C(8)-C(81)	116,2(1,4)
C(31)-C(3)-C(4)	119,8(1,2)	C(41)-C(81)-C(8)	120,4(1,4)
C(3)-C(31)-H(31)	125,7(6,5)	C(1)-C(81)-C(41)	121,2(1,3)
C(3)-C(31)-C(32)	124,1(1,2)	C(1)-C(81)-C(8)	118,4(1,3)

from planarity occurring in the quinone ring, as shown by the endocyclic torsion angles given in Figure 2. This is probably due to the intramolecular close contacts C(23) to C(1) of 3,13 Å and C(23) to O(1) of 3,01 Å. Thus, C(1) and O(1) are displaced by 0,14 and 0,39 Å respectively from the least squares plane containing C(2), C(3), C(4), C(41), and C(81). There are no significant intermolecular close contacts.

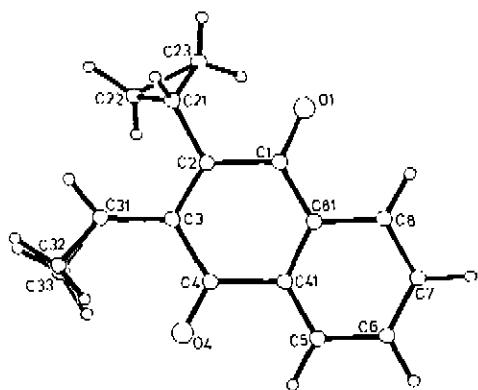


Fig. 1 Perspective view with atomic nomenclature.

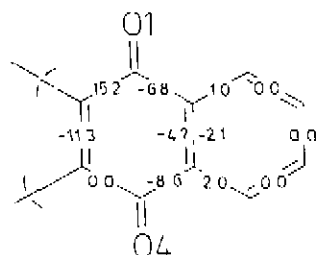


Fig. 2 Endocyclic torsion angles.

Discussion

We have carried out a conformational study of the compound by calculating the van der Waals energy using empirical atom pair potentials. This method of evaluating molecular energies is well established and has recently been reviewed by Kitaigorodsky⁶ and Mirsky.⁷ The coefficients of the atom-atom potentials are of the form

$$U(r) = a \exp(-br) / r^d - c/r^6$$

where r is the distance between any pair of atoms, and the coefficients a , b , c , and d are those given by Giglio,⁸ such that $U(r)$ is evaluated in calories when r is in Å. These potential curves were derived primarily to give good agreement for calculation of molecular position in crystal structure, and the energy values mean little in an absolute sense. No account was taken of possible torsional potentials for the σ -bonds, partial atomic charges, or dipole interactions. The program EENY⁹ calculates molecular coordinates as defined by appropriate torsion angles and sums the energy for all non-bonded pairs of atoms whose separation is dependent upon the torsion angles.

In the present study, if an idealized structure is assumed, in which both the aromatic and quinonoid rings are exactly planar and the cyclopropyl moieties are identical, and the molecule is divided into three residues linked by two torsion angles: τ_1 [C(1)-C(2)-C(21)-H(21)] and τ_2 [C(4)-C(3)-C(31)-H(31)] as shown in Figure 3, then for equal but opposite values of τ_1 and τ_2 , the molecule possesses C_s symmetry, the mirror plane bisecting residue 1 and lying perpendicular to the aromatic and quinonoid rings. Hence, any conformational arrangement defined by torsion angles τ_1 and τ_2 which gives rise to an energy minimum will have an equivalent arrangement at values of $-\tau_1$ and $-\tau_2$, which is its mirror image. The atomic coordinates used in the energy analysis however were not for the idealized molecule, but those obtained from the refined crystal structure.

An energy map was calculated with the torsion angles both varying over the complete angular range 0—360° in 10° increments. This map, shown in Figure 4, yielded six energy minima labelled A,B,C and A',B',C'. These are displayed as a three-dimensional energy surface in Figure 5 for greater clarity.

The torsion angles at the exact minima were obtained using the method of steepest descent incorporated in the

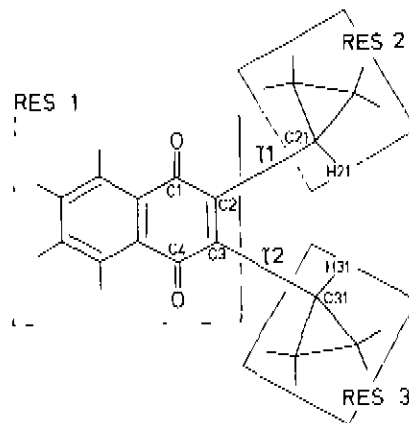
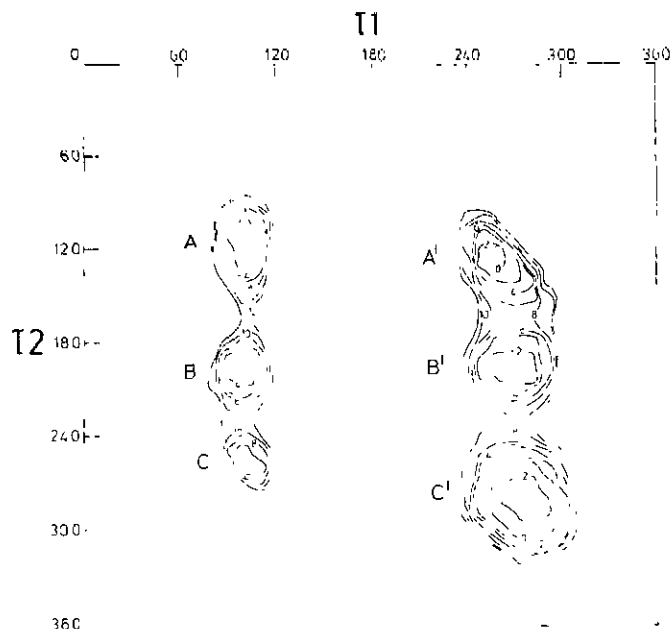
Fig. 3 Schematic representation of torsion angles τ_1 and τ_2 linking the three residues.

Fig. 4 Contour map showing energy minima (kcal).

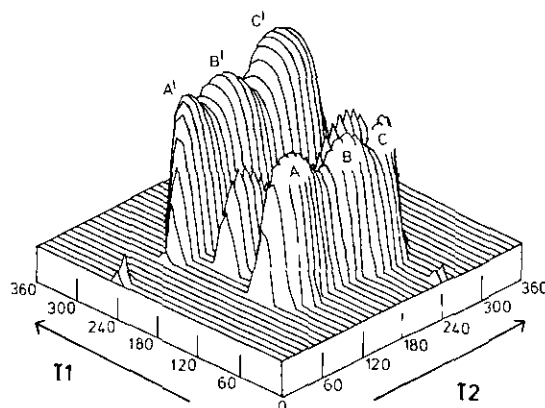


Fig. 5 Three-dimensional energy surface.

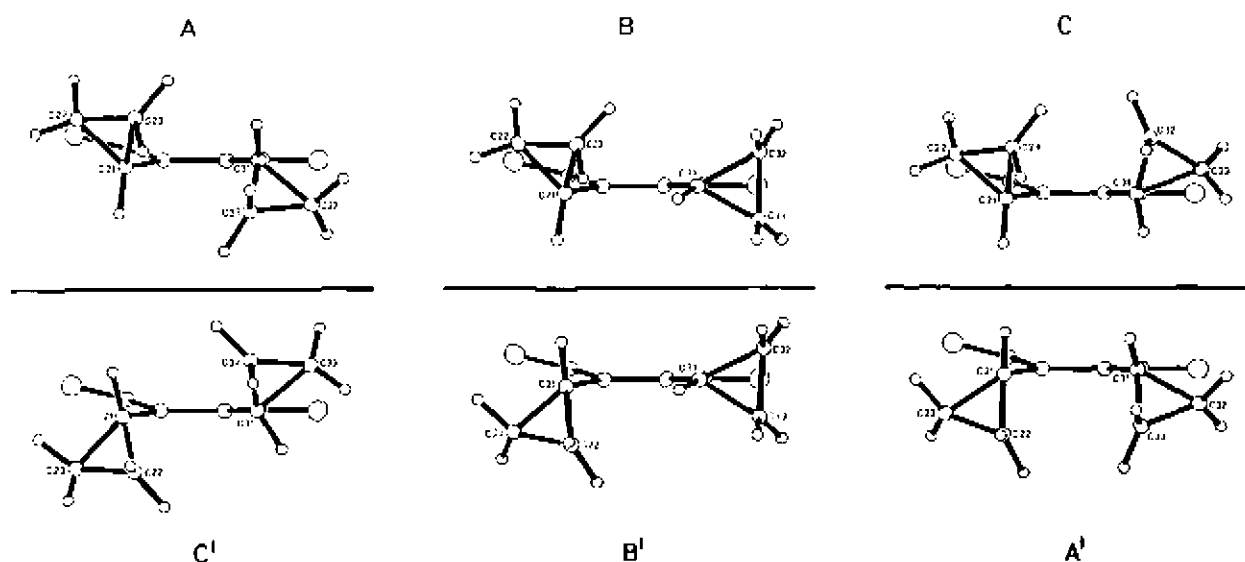


Fig. 6 Molecular conformations corresponding to the energy minima. The view is along a line joining the midpoints of C(2)-C(3) and C(6)-C(7). Aromatic hydrogen atoms and selected carbon atoms have been omitted for clarity.

Table 5 Torsion angles ($^{\circ}$) and energies (kcal) for potential energy minima

	A	B	C	A'	B'	C'
τ_1	100,1	97,8	105,3	261,0	268,7	276,6
τ_2	114,4	198,8	259,2	127,6	195,5	284,8
U_{\min}	-0,4	2,5	3,7	-0,8	0,3	-3,3

program, and these are shown in Table 5 together with calculated energies at these positions. Energy barriers between the different conformations are of the order of 10 kcal mol $^{-1}$. The peaks obtained correspond to the molecular conformations shown in Figure 6, which do indeed display mirror image pairs, although mirror symmetry is inexact. The conformation in the crystal structure with $\tau_1 = 271,3^{\circ}$ and $\tau_2 = 195,4^{\circ}$ is gratifyingly close to that of B' in Figure 6, where $\tau_1 = 268,7^{\circ}$ and $\tau_2 = 195,5^{\circ}$.

As was mentioned above, the room temperature ^1H n.m.r. spectrum of 2,3-dicyclopropyl-1,4-naphthoquinone exhibits a highly symmetrical pattern around the methylene and methine proton absorption region. On heating or cooling the sample, the simple methylene doublet originally present in the spectrum collapses, and the true complexity of the spectrum becomes evident (Figure 7). This temperature dependence is probably due to measurable differences in energy between molecular conformations, described in terms of the torsion angles τ_1 and τ_2 , such that molecules spend a variable length of time in any given conformation relative to another. As the temperature changes, so too does the population distribution, and the ^1H n.m.r. spectrum is accordingly affected. Hence, free rotation about the C(2)-C(21) and C(3)-C(31) bonds is considered to be restricted, in the sense that the barriers separating the energy minima are sufficiently large to ensure that the molecule spends most of its time in those of lowest energy, yet sufficiently small so that interconversion between minima is fast on the n.m.r. time scale.

Figure 8 shows a schematic representation of the methine and methylene chemical shift changes considered to be taking place as a function of temperature. At -35°C , the overall environment of the cyclopropyl rings is such that the

chemical shifts of the Ha and Hb protons are different. The spectrum in this region hence appears as the net resultant of a complicated absorption pattern of the AA'BB'C type, incorporating both vicinal and geminal coupling, and whose interpretation cannot be explained in terms of first-order splitting rules. At room temperature, the conformational population distribution is such that the chemical shift difference between the Ha and Hb protons becomes negligible, i.e. $\delta\text{Ha} = \delta\text{Hb}$ 'by accident',¹⁰ and the spectrum degenerates into a deceptively simple spectrum of the AA'A''A'''C type with a quintet-doublet pattern as observed. The splitting in the multiplets is here an average of the coupling constants involved. As the temperature continues to rise, the chemical shift differences are no longer

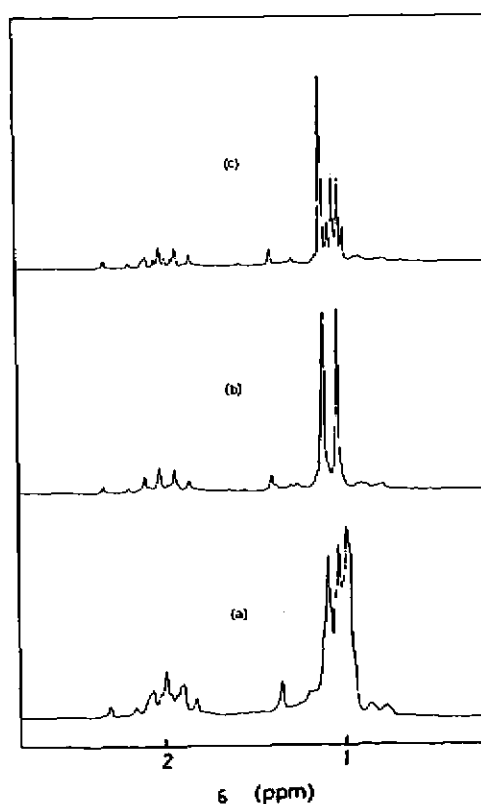


Fig. 7 Methine and methylene ^1H n.m.r. spectrum of 2,3-dicyclopropyl-1,4-naphthoquinone at (a) -35°C , (b) 28°C , and (c) 76°C .

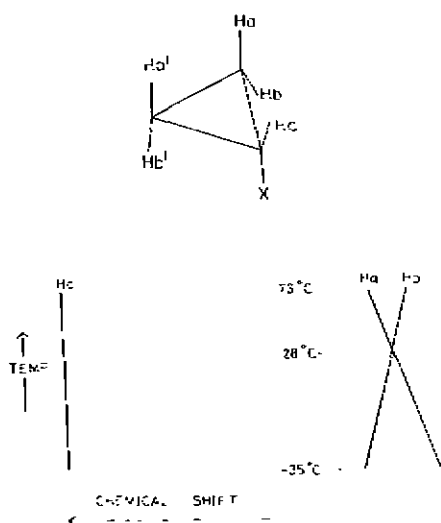


Fig. 8 Schematic representation of the temperature-dependent methine and methylene hydrogen chemical shift changes.

zero and the pattern again becomes complex.

Whether in fact the proton resonances actually 'cross over', as is implied in Figure 8, or merely change direction, can only be ascertained by a complete analysis of the spectra. A detailed analysis could also perhaps yield information as to the nature of the conformational minima, ideally matching those obtained from solid state coordi-

nates, and their relative populations at these differing temperatures.

Supplementary material

Tables of the observed and calculated structure factors (3pp) are available on request from the Photocopying Section, CSIR Library Division, CSTI, P.O. Box 395, Pretoria 0001.

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