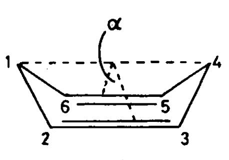
X-Ray Crystallographic Study of the Preferred Conformations of 2,6- and 3,5-Dimethyl-1,4-dihydrobenzoic Acids

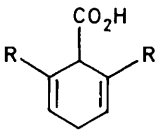
By **Martin C. Grossel**,*† Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY
Anthony K. Cheetham,* **Daniel James**, and **John M. Newsam**, Chemical Crystallography Laboratory, Hooke Building, 9 Parks Road, Oxford OX1 3PD

A single-crystal *X*-ray diffraction study of 2,6-dimethyl-1,4-dihydrobenzoic acid (2b) reveals that the cyclohexadiene ring is somewhat puckered with an angle of pucker, α = 171.6°. Crystals are monoclinic, space group $P2_1/n$, with Z = 4, in a cell with lattice parameters a = 8.922(1), b = 7.890(1), c = 12.251(2) Å, β = 86.57(1)°. 853 Independent reflections gave a final R of 0.044. In contrast, 3,5-dimethyl-1,4-dihydrobenzoic acid (3c) adopts a planar conformation with α = 179.3°. Crystals of (3c) are also monoclinic, space group $P2_1/n$, with Z = 4, in a cell with lattice parameters a = 4.262(1), b = 13.154(1), c = 14.980(2) Å, β = 83.57(1)°. 1 005 Independent reflections gave a final R of 0.047. The conformations observed in the solid state are in close agreement with those deduced from solution ^{1}H n.m.r. data.

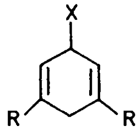
THE use of ^{1}H n.m.r. spectroscopic data as a conformational probe for the cyclohexa-1,4-diene ring has been widely discussed in recent years.[1,2] It is clear from i.r. spectroscopic studies [3] that, in the gas phase, the parent hydrocarbon (1) exists in a shallow potential-energy well with an energy minimum corresponding to a planar geometry. However, the temperature dependence of the ^{1}H n.m.r. homoallylic coupling constants suggests that there is a significant population of higher vibrational energy levels at room temperature; [4] this complicates the interpretation of the n.m.r. data. ‡



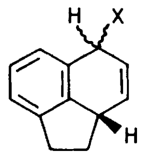
(1)



	R
(2) a ;	H
b ;	Me
c ;	MeO



	R	X
(3) a ;	H	CH$_2$OH
b ;	Me	CH$_2$OH
c ;	Me	CO$_2$H



	X
(4) a ;	CO$_2$H
b ;	CH$_2$OH
c ;	CMe$_2$•OH

The 1,4-dihydrobenzoic acids (2) have been studied extensively,[1,5] and their ^{1}H n.m.r. spectra are readily interpretable because of the markedly different chemical shifts of the protons on C-1 and C-4. From a detailed analysis of the spectra of the 2,6-dimethyl- and 2,6-dimethoxy-1,4-dihydrobenzoic acids, (2b) and (2c) respectively, it was originally suggested [1] that both adopt an essentially planar conformation and that the reduced magnitude of the homoallylic couplings in these systems arises from an electronic substituent effect. This proposal has recently been challenged [5] on the grounds that the introduction of C-3 and C-5 methyl substituents into 1,4-dihydrobenzyl alcohol (3a) has little effect upon the magnitudes of the homoallylic coupling constants. The reduced couplings in (2b) and (2c) may therefore result from slight puckering of the cyclohexadienyl rings. Since the interpretation of n.m.r. coupling-constant data in these systems has not yet been shown to give definitive conformational information, we have now determined the crystal structures of the 2,6- and 3,5-dimethyl-1,4-dihydrobenzoic acids (2b) and (3c).

EXPERIMENTAL

Preparations.—2,6-*Dimethyl*-1,4-*dihydrobenzoic Acid* (2b). This was prepared as previously described [1] and recrystallised from light petroleum (b.p. 60—80 °C) as colourless plates, m.p. 105 °C (lit.,[6] 104—106 °C).

3,5-*Dimethyl*-1,4-*dihydrobenzoic Acid* (3c). To a solution of 3,5-dimethylbenzoic acid (5.0 g, 0.033 mol) in dry ether (50 ml) and dry liquid ammonia (200 ml) was added sodium (5 g, 0.22 mol). The resulting blue solution was stirred for ½ h and then quenched with ammonium chloride (12 g, 0.22 mol). The ammonia was allowed to evaporate under a stream of nitrogen, the residue acidified, and the aqueous solution extracted with ether (3 × 100 ml). The combined extracts were dried (MgSO$_4$) and solvent was removed under reduced pressure. The residual solid was crystallised from light petroleum (b.p. 60—80 °C) to give 3,5-dimethyl-1,4-dihydrobenzoic acid [5] (4.4 g, 88%), as colourless needles, m.p. 105 °C, τ (CDCl$_3$) − 1.5br (1 H, s, OH), 4.49br (2 H, m, =CH), 6.25br (1 H, m, C*H*–CO), 7.40br (2 H, d, CH$_2$), and 8.23br (6 H, s, CH$_3$); $\nu_{max.}$ (CHCl$_3$) 3 600—2 450 (CO$_2$H), 1 710 cm^{-1} (C=O) (Found: C, 71.00; H, 7.85. C$_9$H$_{12}$O$_2$ requires C, 71.05; H, 7.89%).

^{1}H *N.m.r. Spectra.*—90 MHz Spectra were recorded on a Perkin-Elmer R32 spectrometer. 220 MHz Spectra were measured by the P.C.M.U., Harwell, whom we thank. Double-resonance experiments at both operating frequencies

† *Present address:* Department of Chemistry, Bedford College, University of London, Regent's Park, London NW1 4NS.

‡ An ambiguity in the wording of the abstract of ref. 1 has led to some misunderstanding of this point, resulting, for example, in the conclusion [5] that 'flat cyclohexa-1,4-dienes could well exist as rapidly equilibrating boat conformations.' There seems little doubt that the energy minimum conformation of cyclohexa-1,4-diene is planar, but when long time-scale spectroscopic techniques are employed the effect of molecular vibrations must also be taken into account; see *e.g.* N. L. Allinger, *Adv. Phys. Org. Chem.*, 1976, **13**, 49, and O. Ermer, *Structure and Bonding*, 1976, **27**, 196.

(in particular decoupling the methyl group resonances) aided measurement of the various couplings. The methyl-decoupled spectra were simulated at both spectrometer frequencies by use of the program NMRCAL on a Nicolet B NC 12 computer.

3,5-*Dimethyl*-1,4-*dihydrobenzoic Acid* (3c).—*Crystal data.* $C_9H_{12}O_2$. Monoclinic, $M = 152$, $a = 4.262(1)$, $b = 13.154(1)$, $c = 14.980(2)$ Å, $\beta = 83.57(1)°$, $U = 834.6$ Å^3, $D_m = 1.2$ g cm^{-3} (by flotation), $D_c = 1.2$ g cm^{-3} for $Z = 4$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ (Mo-K_α) = 0.9 cm^{-1}. Space group $P2_1/n$.

Initial survey photographs exhibited the systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ which indicated space group $P2_1/n$ with b unique. A selected crystal (*ca.* 0.25 mm cube) was then mounted on an Enraf-Nonius CAD 4F diffractometer. An approximate orientation matrix was derived from the co-ordinates of 20 reflections observed in a rotation exposure, which were automatically centred. The orientation matrix and unit-cell parameters were optimised by a least-squares refinement using the angular co-ordinates of 25 reflections with $16° < \theta < 19°$. Automatic data collection was implemented using bisecting geometry in the range $0 < \theta < 30°$. The angular co-ordinates of three reflections and the intensities of a further three were monitored throughout data collection to provide a check on variations in crystal orientation and intensity. In all, 3 958 reflections were measured. Three absorption curves were collected, but these indicated that a correction was unnecessary. Lorentz and polarisation corrections were applied and the data merged to give 1 005 independent structure amplitudes with $I > 3\sigma(I)$, where I is the final observed intensity and $\sigma(I)$ the standard deviation derived from counting statistics. The structure was solved by direct methods using MULTAN.[7] Full-matrix least-squares techniques were employed for the refinement.[8] All hydrogen atoms were apparent in a difference Fourier synthesis. In the final cycles of refinement of positional and anisotropic temperature factors (isotropic only for hydrogen atoms), a three-term Chebyshev series was used for the weighting scheme. A final R of 0.047 (R' 0.062) was obtained. Atom co-ordinates are given in Table 1, bond lengths and angles in Tables 2 and 3. For both compounds (2b) and (3c), final observed and calculated structure factors, and thermal parameters for carbon, hydrogen, and oxygen are listed in Supplementary Publication No. SUP 22641 (22 pp.).* The crystallographic atom

TABLE 1

Fractional atom co-ordinates in 3,5-dimethyl-1,4-dihydrobenzoic acid (3c), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
(*a*) Carbon and oxygen atoms			
C(1)	−0.185 4(5)	0.469 5(2)	0.284 3(1)
C(2)	−0.060 2(6)	0.372 7(2)	0.241 2(1)
C(3)	0.129 2(5)	0 367 7(2)	0.164 9(1)
C(4)	0.243 2(5)	0.461 8(2)	0.115 2(1)
C(5)	0.121 2(5)	0.559 8(2)	0 156 3(1)
C(6)	−0.071 9(5)	0.562 3(2)	0.232 2(1)
C(7)	−0.107 2(5)	0.479 2(2)	0.380 0(1)
C(8)	0.232 7(7)	0.654 6(2)	0.106 4(2)
C(9)	0.244 5(7)	0.268 8(2)	0.123 7(2)
O(1)	0.063 9(5)	0.420 0(1)	0.413 9(1)
O(2)	−0.239 8(5)	0.556 6(1)	0.423 1(1)
(*b*) Hydrogen atoms			
H(1)	−0.426(6)	0.469(2)	0.288(2)
H(2)	−0.119(6)	0.313(2)	0.272(2)
H(4)	0.193(6)	0.458(2)	0.052(2)
H(5)	0.482(7)	0.462(2)	0.112(2)
H(6)	−0.153(7)	0.630(2)	0.254(2)
H(81)	0.168(5)	0.652(2)	0.047(2)
H(82)	0.142(5)	0.714(2)	0.136(2)
H(83)	0.468(8)	0.659(2)	0.102(2)
H(91)	0.175(5)	0.214(2)	0.161(2)
H(92)	0.161(5)	0.262(2)	0.063(2)
H(93)	0.482(7)	0.269(2)	0.115(2)
H(OH)	−0.174(9)	0.564(3)	0.482(2)

TABLE 2

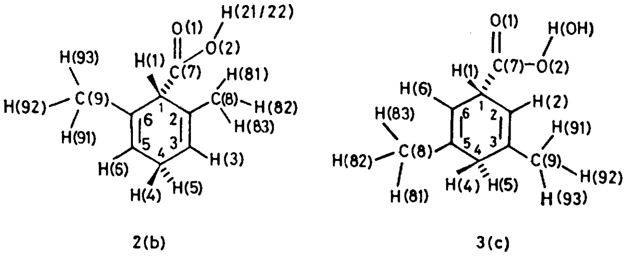
Bond lengths (Å), with estimated standard deviations in parentheses, for (3c)

C(1)–C(2)	1.498(3)	C(1)–H(1)	1.02(3)
C(1)–C(6)	1.501(3)	C(2)–H(2)	0.93(2)
C(1)–C(7)	1.513(3)	C(4)–H(4)	1.00(2)
C(2)–C(3)	1.325(3)	C(4)–H(5)	1.01(3)
C(3)–C(4)	1.497(3)	C(6)–H(6)	0.99(2)
C(3)–C(9)	1.499(3)	C(8)–H(81)	0.97(3)
C(4)–C(5)	1.496(3)	C(8)–H(82)	0.96(3)
C(5)–C(6)	1.326(3)	C(8)–H(83)	1.00(3)
C(5)–C(8)	1.504(3)	C(9)–H(91)	0.94(3)
C(7)–O(1)	1.216(3)	C(9)–H(92)	1.01(3)
C(7)–O(2)	1.301(3)	C(9)–H(93)	1.01(3)
		O(2)–H(OH)	0.96(3)

TABLE 3

Bond angles (°) for (3c)

C(1)–C(2)–C(3)	124.6(2)	C(4)–C(5)–C(8)	115.8(2)
C(1)–C(6)–C(5)	123.9(2)	C(4)–C(3)–C(9)	116.0(2)
C(2)–C(1)–C(6)	112.9(2)	C(6)–C(1)–C(7)	109.4(2)
C(2)–C(1)–C(7)	112.0(2)	C(6)–C(5)–C(8)	122.4(2)
C(2)–C(3)–C(4)	121.3(2)	O(1)–C(7)–C(1)	123.2(2)
C(2)–C(3)–C(9)	122.6(2)	O(1)–C(7)–O(2)	122.8(2)
C(3)–C(4)–C(5)	115.4(2)	O(2)–C(7)–C(1)	114.0(2)
C(4)–C(5)–C(6)	121.9(2)		



2(b) 3(c)

FIGURE 1 Numbering scheme used for crystallographic analysis

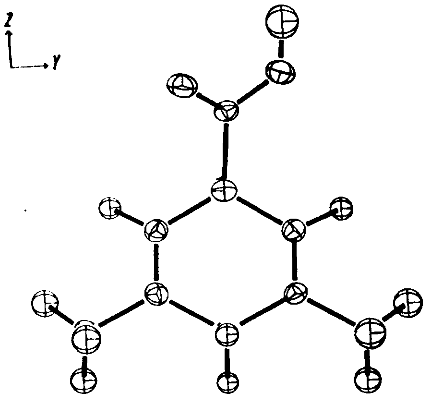


FIGURE 2 The molecule of (3c) from above the plane of the molecule

---

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

numbering is shown in Figure 1 and drawings of the molecule in Figures 2 and 3.

2,6-*Dimethyl*-1,4-*dihydrobenzoic Acid* (2b).—$C_9H_{12}O_2$. Monoclinic, $M = 152$, $a = 8.922(1)$, $b = 7.890(1)$, $c = 12.251(2)$ Å, $\beta = 86.57(1)°$, $U = 860.9$ Å^3, $D_m = 1.2$ g cm^{-3} (by flotation), $D_c = 1.2$ g cm^{-3} for $Z = 4$. μ (Mo-K_α) = 0.9 cm^{-1}. Space group $P2_1/n$.

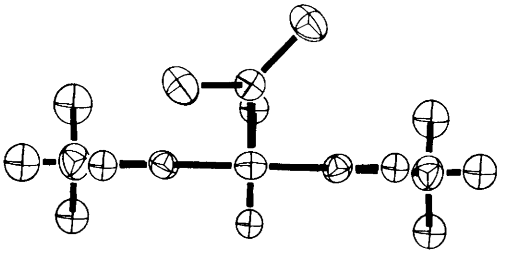


FIGURE 3 The molecule of (3c) viewed along the C(1) · · · C(4) axis

Initial survey photographs exhibited systematic absences *h0l*, $h + l = 2n + 1$; *0k0*, $k = 2n + 1$, consistent with space group $P2_1/n$ (*b* unique). A selected crystal (*ca.* 0.3 mm cube) was mounted as before. The alignment and data collection were carried out as already described. 3 670 reflections were measured in the range $0 < \theta < 30°$. Absorption curves were also collected, but these indicated that no correction was necessary. Lorentz and polarisation corrections were applied, and the data were merged to give 853 independent reflections having $I > 3\sigma(I)$. The structure was solved [7] and refined [8] as before. Hydrogen atoms, with the exception of that in the carboxylic acid group, were found from an electron-density difference Fourier synthesis. Slant Fourier calculations suggest that the acid hydrogen is disordered over two positions, and thus hydrogen atoms were placed in those positions with occupancy ½. In the final refinement, the co-ordinates and anisotropic temperature factors of the carbon and oxygen atoms were refined with the co-ordinates and isotropic temperature factors of the hydrogen atoms; the co-ordinates of the acid hydrogen were fixed. A three-term Chebyshev series was used as a weighting scheme. A final *R* value of 0.044 (*R'* 0.044) was reached. Atom co-ordinates are listed in Table 4, bond lengths and bond angles in Tables 5 and 6 respectively. Drawings of the molecule are shown in Figures 4 and 5.

TABLE 4

Fractional atom co-ordinates for 2,6-dimethyl-1,4-dihydrobenzoic acid (2b), with estimated standard deviations in parentheses

(*a*) For carbon and oxygen atoms

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.065 6(3)	0.166 6(3)	0.823 5(2)
C(2)	0.203 8(2)	0.210 3(3)	0.751 4(2)
C(3)	0.195 7(4)	0.232 1(3)	0.645 4(2)
C(4)	0.055 7(4)	0.216 4(5)	0.586 2(2)
C(5)	−0.072 5(3)	0.151 1(3)	0.655 3(2)
C(6)	−0.072 9(3)	0.128 2(3)	0.761 9(2)
C(7)	0.033 3(2)	0.311 3(3)	0.903 3(2)
C(8)	0.347 2(4)	0.225 5(4)	0.808 9(4)
C(9)	−0.204 7(4)	0.062 6(5)	0.830 6(3)
O(1)	0.074 1(2)	0.298 2(2)	0.999 0(1)
O(2)	−0.032 1(2)	0.440 0(2)	0.869 1(1)

(*b*) For hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*
H(1)	0.087(3)	0.067(4)	0.869(2)
H(3)	0.287(4)	0.259(4)	0.601(3)
H(4)	0.074(4)	0.146(4)	0.524(3)
H(5)	0.032(5)	0.326(5)	0.551(3)
H(6)	−0.161(3)	0.125(4)	0.620(2)
H(81)	0.426(5)	0.233(5)	0.760(3)
H(82)	0.365(5)	0.127(6)	0.835(3)
H(83)	0.335(4)	0.318(5)	0.863(3)
H(91)	−0.278(4)	0.035(4)	0.784(3)
H(92)	−0.240(5)	0.152(6)	0.883(4)
H(93)	−0.169(5)	−0.046(6)	0.871(4)

TABLE 5

Bond lengths (Å), with estimated standard deviations in parentheses for (2b)

C(1)–C(2)	1.512(3)	C(1)–H(1)	0.99(3)
C(1)–C(6)	1.517(3)	C(3)–H(3)	0.97(3)
C(1)–C(7)	1.520(3)	C(4)–H(4)	0.95(4)
C(2)–C(3)	1.316(4)	C(4)–H(5)	1.00(4)
C(2)–C(8)	1.502(4)	C(5)–H(6)	0.95(3)
C(3)–C(4)	1.488(5)	C(8)–H(81)	0.90(4)
C(4)–C(5)	1.474(4)	C(8)–H(82)	0.86(5)
C(5)–C(6)	1.318(4)	C(8)–H(83)	0.99(4)
C(6)–C(9)	1.497(4)	C(9)–H(91)	0.93(4)
C(7)–O(1)	1.253(3)	C(9)–H(92)	0.99(5)
C(7)–O(2)	1.255(3)	C(9)–H(93)	1.05(5)

TABLE 6

Bond angles (°) for (2b)

C(1)–C(2)–C(3)	121.0(2)	C(3)–C(4)–C(5)	113.3(3)
C(1)–C(2)–C(8)	115.6(3)	C(4)–C(5)–C(6)	124.9(2)
C(1)–C(6)–C(5)	120.8(2)	C(5)–C(6)–C(9)	124.1(2)
C(1)–C(6)–C(9)	115.2(3)	C(6)–C(1)–C(7)	110.0(2)
C(2)–C(1)–C(6)	114.5(2)	O(1)–C(7)–C(1)	119.0(2)
C(2)–C(1)–C(7)	108.7(2)	O(1)–C(7)–O(2)	123.1(2)
C(2)–C(3)–C(4)	124.6(3)	O(2)–C(7)–C(1)	117.9(2)
C(3)–C(2)–C(8)	123.4(3)		

DISCUSSION

Rabideau and co-workers [5] have deduced the solution conformation of 2,6-dimethyl-1,4-dihydrobenzoic acid (2b) from a comparison of its ^1H n.m.r. data with that of 3,5-dimethyl-1,4-dihydrobenzyl alcohol (3b). However, two problems arise from such an approach. The data for the former compound were obtained in the presence of a shift reagent, and it is clearly possible that interactions in the complex may distort the conformation of the cyclohexadiene ring. Further the effect of a change of the C-1 substituent from $-CH_2OH$ to $-CO_2H$ on the magnitudes of the couplings must be considered. We have therefore carried out a detailed analysis of the ^1H n.m.r. spectrum of 3,5-dimethyl-1,4-dihydrobenzoic acid (3c) at both 90 and 220 MHz. The values of the coupling constants obtained (see Table 7) are identical with those reported [5] for the related dihydrobenzyl alcohol (3b). Further, the magnitude of the *cis*- and *trans*-homoallylic couplings in 5-substituted 2a,5-dihydroacenaphthenes (4) is unaffected by a change of the C-5 substituent from carboxy (4a) to hydroxymethyl (4b, c).[9-11] We therefore consider that neither of these effects complicates the interpretation of the data.

The crystal structure of 3,5-dimethyl-1,4-dihydrobenzoic acid (3c) reveals that the cyclohexadiene ring is indeed essentially planar (α * = 179.3°) (Figures 2 and 3,

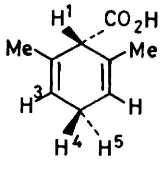
---

* The angle α is that angle between the planes defined by C(1)–C(2)–C(3)–C(4) and C(4)–C(5)–C(6)–C(1) in a 1,4-dihydrobenzene ring (see ref. 1).

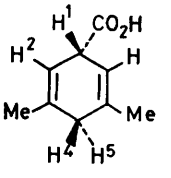
and Tables 1—3). In contrast, 2,6-dimethyl-1,4-dihydrobenzoic acid (2b) adopts a slightly puckered conformation with $\alpha = 171.6°$ (Figures 4 and 5, and Tables 4—6), in agreement with the more recent analysis of the solution n.m.r. data for this compound.[5]

TABLE 7

Coupling constants (Hz) measured [a] and calculated [b] (using the crystallographic data reported in this work) for the ring protons in 2,6- and 3,5-dimethyl-1,4-dihydrobenzoic acids



(2b)



(3c)

J	Obs. [c]	Calc. [d]		Obs.	Calc. [d]	
1,2				3.6	3.3 [e,f]	4.2 [g]
1,3	−0.8	−0.7 [h]	−1.5 [g]			
1,4 (*cis*)	6.0	4.05 [c]	12.4 [g]	8.1	5.65 [c]	16.0 [g]
1,5 (*trans*)	6.25	5.95 [c]	11.9 [g]	7.1	6.35 [c]	12.5 [g]
2,4				−1.7	−1.4 [h]	−2.2 [g]
2,5				−1.7	−1.6 [h]	−2.3
3,4	4.0	4.0 [e,f]	4.9 [g]			
3,5	3.25	2.8 [e,f]	3.4 [g]			
4,5	−22.2			−23.6		
	±0.2 Hz			±0.2 Hz		

[a] Experimental values were obtained by computer simulation of the 90 and 220 MHz spectra in $CDCl_3$ solution. [b] References for each calculated value refer to the particular theoretical data used in each case. [c] Ref. 1. [d] Derived using the value of α obtained from the crystallographic structures. [e] Ref. 11. [f] Ref. 13. [g] Ref. 12. [h] Ref. 9.

There are details in the literature of various calculations relating to the conformational dependence of allylic and homoallylic couplings about the cyclohexa-1,4-diene ring.[1,5,9,12] We have used these data to predict various coupling constants which should be observed if 2,6- and 3,5-dimethyl-1,4-dihydrobenzoic acid adopt their crystallographic conformations in solution. These results are also presented in Table 7 in order to allow a direct comparison with the experimental values. We have also estimated the vicinal couplings using calculations of Pople and co-workers.[13] It will be seen that both vicinal and allylic couplings are in close agreement with the experimental values. The vicinal coupling data also support the original assignments of H-4 and H-5 as *cis* and *trans* respectively to H-1 in the 2,6-dimethyl acid (2b) for, in a boat conformation in which the carboxy-substituent is pseudoaxial, the pseudoequatorial proton at C-4 will be the more strongly coupled to H-3.

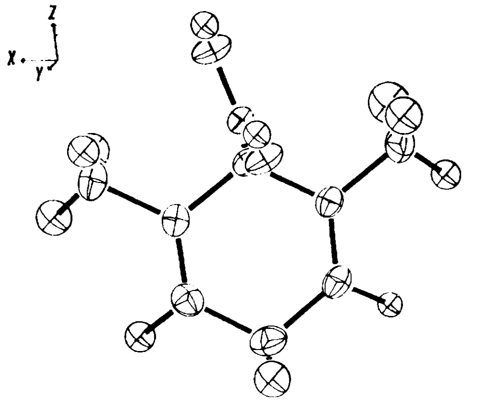


FIGURE 4 The molecule of (2b) from above the plane of the molecule

In contrast, neither set of values for the predicted homoallylic couplings bears close comparison with the experimental data, even when the more recent calculations [5,12] are scaled down by a factor of two. † Rabideau and co-workers [2,5] have, however, suggested that J_{cis}/J_{trans} ratios of homoallylic couplings should provide a more satisfactory probe into the conformation of cyclohexa-1,4-dienes. Our results would seem to support this proposal, for whilst the J_{cis}/J_{trans} ratio for the planar 3,5-dimethyl acid is 1.14 this falls to 0.96 for the more puckered 2,6-dimethyl acid. The suggestion [5] that the ratio of homoallylic couplings in these systems is a more sensitive probe into molecular conformation than the actual magnitudes of the couplings themselves is thus supported by our results and merits further study.

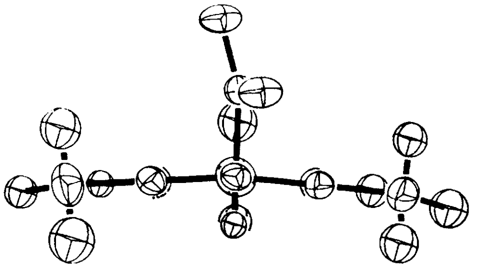


FIGURE 5 The molecule of (2b) viewed along the C(1) · · · C(4) axis

† If the calculations of Marshall and co-workers [12] are compared directly with those from our earlier data [1] it is found that whilst both sets of results give essentially the same form for the geometric dependence of homoallylic coupling, those of Marshall are consistently too large by a factor of 2 when compared with experiment. From a direct comparison of the two sets of data we can find no evidence for a special conformationally dependent ' dual-path ' effect claimed by Marshall.[12] This will be discussed in more detail elsewhere.[11]

In conclusion we have found that the conformations of the simple, flexible cyclohexa-1,4-dienes (2b) and (3c) as determined by *X*-ray diffraction closely resemble those suggested by solution ^{1}H n.m.r. coupling-constant data. Our results also demonstrate that *cis*/*trans* homoallylic coupling constant ratios may provide a sensitive probe into ring conformation. We are currently studying substituent effects on the conformations of other flexible dihydroaromatic compounds.

We thank the Dean, Canons, and Students of Christ Church, Oxford for a research fellowship to M. C. G., and P. Glover for assistance in the crystallographic work.

[9/545 *Received, 4th January,* 1979]

REFERENCES

[1] M. C. Grossel and M. J. Perkins, *J.C.S. Perkin II*, 1975, 1544, and refs. therein.

[2] P. W. Rabideau, *Accounts Chem. Research*, 1978, **11**, 141.

[3] J. Laane and R. C. Lord, *J. Mol. Spectroscopy*, 1971, **39**, 340.

[4] M. C. Grossel and M. J. Perkins, *Nouveau J. Chem.*, 1979, **3**, 285.

[5] P. W. Rabideau, J. W. Paschal, and J. L. Marshall, *J.C.S. Perkin II*, 1977, 842.

[6] H. van Bekkum, C. B. Van der Bosch, G. Van Minnen-Pathuis, J. C. De Mos, and A. M. Van Wijk, *Rec. Trav. chim.*, 1971, **90**, 137.

[7] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[8] J. R. Carruthers, *CRYSTALS* User Manual, 1975, Oxford University Computing Laboratory.

[9] M. C. Grossel and R. C. Hayward, *J.C.S. Perkin II*, 1976, 851.

[10] P. W. Rabideau, E. G. Burkholder, M. J. Yates, and J. W. Paschal, *J. Amer. Chem. Soc.*, 1977, **99**, 3596.

[11] M. C. Grossel, to be published.

[12] J. L. Marshall, L. G. Faehl, C. R. McDaniel, jun., and N. D. Ledford, *J. Amer. Chem. Soc.*, 1977, **99**, 321.

[13] G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem., Soc.* 1970, **92**, 4497.