

References

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Tricyclo[18.2.2.2^{2,5}]hexacos-1(22),2,4,20,23,25-hexaene ([14.0]-*p*-Cyclophane)

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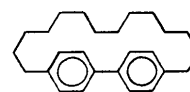
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Abstract. C₂₆H₃₆, *M_r* = 348.6, monoclinic, *C2/c*, *a* = 23.986 (9), *b* = 7.844 (3), *c* = 11.415 (4) Å, β = 92.29 (3)°, *V* = 2146 (1) Å³, *Z* = 4, *D_x* = 1.08 g cm⁻³, Mo *Kα*, λ = 0.71073 Å, μ = 0.56 cm⁻¹, *F*(000) = 768, *T* = 297 K, final *R* = 0.054 for 1162 observed reflections. The title compound is established by an X-ray study to have a twofold axis coinciding with a crystallographic twofold axis, and to be in a different conformation in the crystal from that observed in solution by NMR studies. NMR and molecular mechanics calculations suggest that the solution conformation is a roughly equal mixture of the X-ray structure with a more twisted biphenyl system and a slightly more stable conformation which does not pack as well as the X-ray conformation.

Introduction. The title compound (1) was first prepared by Nakazaki & Yamamoto (1965), who observed that it had proton absorptions in the NMR as far upfield as 0.6, indicating that some of the methylene protons are strongly shielded owing to their position above the benzene ring. We recently found a better route to (1) (to be published elsewhere), and now wish to report the results of an X-ray diffraction study on a crystal of (1) and to compare the conformation observed in the

crystal with what is indicated by NMR and molecular mechanics calculations to be present in solution.



(1)

Experimental. Colorless crystals grown by slow evaporation from pentane at 263 K. Crystal dimensions 0.4 × 0.4 × 0.4 mm. Syntex P2₁ diffractometer. Cell constants from 25 reflections with 13 ≤ 2θ ≤ 24°. Systematic absences: *hkl*, *h* + *k* = 2*n* + 1, *h0l*, *l* = 2*n* + 1. 2θ_{max} = 50°. Range of *hkl*: 0→28, 0→9, -13→13. Scan rate 3–29°. Two check reflections every 98 data points showed 0.4% average decay; no decay or absorption correction. 1162 of 1891 reflections with *I* > 2.5σ(*I*) used in *F*² full-matrix refinement, *R*_{int} = 0.012. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) using 224 highest *E* values; all non-H atoms found in first *E* map. Refinement of non-H atoms with isotropic temperature factors gave *R* = 0.10; final refinement (118 parameters) of non-H atoms with anisotropic temperature factors after adding H atoms in calculated positions with isotropic temperature factors

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of 5.0 Å², $R = 0.054$, $wR = 0.061$, $S = 2.3$, weighting scheme of Corfield, Doedens & Ibers (1967), with $p = 0.03$. $(\Delta/\sigma)_{\max} = 0.01$. $\Delta\rho = -0.3 \rightarrow 0.2 \text{ e \AA}^{-3}$. No anomalous-dispersion or extinction corrections. Atomic scattering factors from Cromer & Waber (1974). Programs *SDP* (Frenz, 1978), including plotter program *ORTEPII* (Johnson, 1976), run on PDP11/34a.

NMR parameters of (1) in CDCl₃, 600 MHz (Carnegie-Mellon University), with ¹H assignments established by ¹H-¹H decoupling: ¹H $\delta 7.56 \sim d[8.2 \text{ Hz, HC(2)]$, $7.23 \sim d[8.2 \text{ Hz, HC(3)]$, $2.68m[\text{HC(7)}]$, $1.65 \sim p[6 \text{ Hz, HC(8)]$, $1.16 \sim p[6 \text{ Hz, HC(9)]$, $0.84p[6 \text{ Hz, HC(11)]$, $0.71p[6 \text{ Hz, HC(10)]$, $0.62m[\text{HC(13)}]$, $0.53m[\text{HC(12)}]$. ¹³C $\delta 141.9[\text{C(4)}]$; $138.5[\text{C(1)}]$; $130.0[\text{C(3)}]$; $126.7[\text{C(2)}]$; $35.5[\text{C(7)}]$; $30.8[\text{C(8)}]$; $29.5, 28.9, 28.8, 28.4$ and $26.5 [\text{C(9)-C(13)}]$.

Discussion. Fig. 1(a) shows a molecule of (1) in the crystal and Table 1 gives the final positional and equivalent isotropic temperature factors.* The molecule in the crystal has a twofold axis, and a conformation in which the protons of several of the methylenes should clearly experience upfield NMR shifts owing to their lying over the aromatic rings. To understand better what conformations are preferred in solution, we calculated a local-minimum-energy structure *in vacuo* from this X-ray structure using *MMPMI*, a molecular mechanics program based on *MMP1* and *MM2*, and taking π overlap into account (Serena Software, Bloomington, IN 47402-3076). In this 'MMPMI-minimized X-ray structure', depicted in Fig. 1(b), the main change is the increased angle of twist about the biphenyl system from the 12.4(2)° observed in the crystal to 39°. This change, which we calculate from *MMPMI* would lower the energy in biphenyl itself by 10.5 kJ mol⁻¹, is substantiated by the upfield location of the C(2) proton absorption in the NMR (we calculate that a 12° twist would give $\delta 7.78$, whereas the observed $\delta 7.56$ corresponds to a 34° twist). As the NMR chemical shifts of the methylene protons calculated using the tables of Johnson & Bovey (1958) from this minimized structure do not fit very well what is observed in solution (Table 2), we tried using molecular models to find comparable or better local-minimum-energy conformations for (1) which would be present in appreciable amounts in solution. The conformation shown in Fig. 1(c), with seven *anti* arrangements of the carbon chain from the C(10)-C(11) bond through the C(10')-C(11') bond [the X-ray structure also has seven *anti* arrangements in the chain, but about the C(8)-C(9) and C(8')-C(9')]

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and coordinates for the *MMPMI* conformations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43454 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

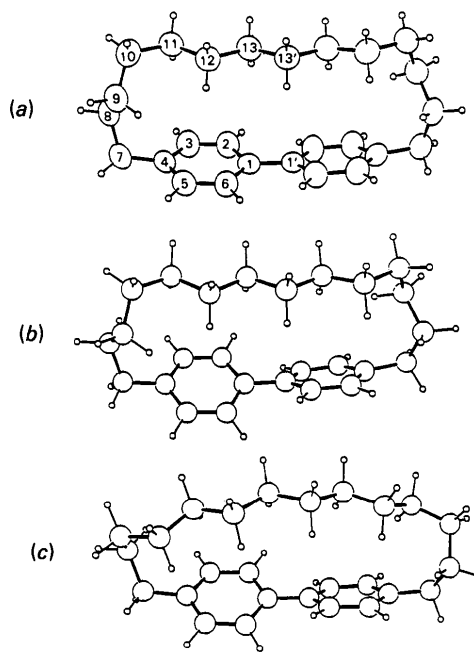


Fig. 1. (a) ORTEP view of a molecule of (1) in the crystal, with 50% probability thermal ellipsoids for C atoms and arbitrary spheres for H atoms. (b) ORTEP view of the *MMPMI*-minimized X-ray conformation of (1), with arbitrary spheres for C and H atoms. (c) ORTEP view of the conformation of (1) calculated using *MMPMI* to be most stable, with arbitrary spheres for C and H atoms.

Table 1. Positional parameters and their *e.s.d.*'s

$$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	0.52921 (9)	0.1839 (3)	0.2305 (2)	4.01 (5)
C(2)	0.5744 (1)	0.2033 (4)	0.3098 (2)	5.13 (6)
C(3)	0.6281 (1)	0.2148 (4)	0.2736 (2)	5.34 (6)
C(4)	0.6405 (1)	0.2086 (3)	0.1563 (2)	4.40 (5)
C(5)	0.5961 (1)	0.1825 (4)	0.0779 (2)	5.26 (6)
C(6)	0.5421 (1)	0.1708 (4)	0.1141 (2)	5.07 (6)
C(7)	0.6987 (1)	0.2410 (3)	0.1170 (2)	5.10 (6)
C(8)	0.7164 (1)	0.4247 (4)	0.1397 (2)	5.10 (6)
C(9)	0.6840 (1)	0.5529 (4)	0.0629 (2)	5.35 (6)
C(10)	0.6743 (1)	0.7235 (4)	0.1207 (2)	5.49 (6)
C(11)	0.6324 (1)	0.7196 (3)	0.2170 (2)	5.11 (6)
C(12)	0.5719 (1)	0.6943 (3)	0.1754 (2)	5.16 (6)
C(13)	0.5305 (1)	0.6963 (3)	0.2711 (2)	4.96 (6)

Table 2. Observed and calculated NMR chemical shifts (δ) of HC(10)-HC(13) in (1)

Protons	Calculated for	Calculated for	Average	Observed
	minimized	<i>MMPMI</i> min.		
	X ray structure	energy structure		
HC(10)	1.05	0.68	0.86	0.71
HC(11)	0.94	0.60	0.77	0.84
HC(12)	0.22	0.27	0.25	0.53
HC(13)	0.63	0.61	0.62	0.62

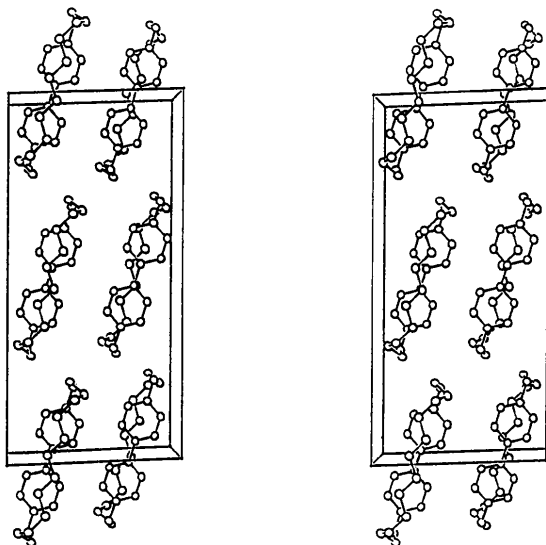


Fig. 2. ORTEP view of a unit cell, *a* axis vertical, perpendicular to *b*.

bonds rather than about the C(10)—C(11) and C(10')—C(11') bonds] and twist angle 34° , was the only one of many tried which had a smaller calculated strain energy ($114.5 \text{ kJ mol}^{-1}$) than the X-ray structure ($115.3 \text{ kJ mol}^{-1}$); all others were at least 7.1 kJ mol^{-1} higher than the X-ray structure. The methylene proton chemical shifts calculated for this 'lowest-energy structure' are also shown in Table 2. They do not give a very good fit to the experimental values, but a roughly equimolar mixture with the MMPMI-minimized X-ray structure, which is what would be expected if these two conformations are the most stable but differ very little in energy, comes fairly close (Table 2); the discrepan-

cies may be due to lesser amounts of other less stable conformations.

Fig. 2 shows how the molecules pack in the crystal; apparently the conformation observed in the crystal gives better packing than the minimum-energy-solution conformation. The crystal consists of equimolar amounts of right- and left-handed molecules, stacked through the crystal in the *y* direction with the roughly flat aromatic rings above the methylene chains of the adjacent molecules in the stack; as can be seen in Fig. 1, the methylene chains in the molecules in the crystal, unlike those of the minimum-energy conformation, have a slightly concave arrangement which fits well with the slightly convex shape for the aromatic rings. The decrease in the angle of twist within the biphenyl system in the molecules in the crystal no doubt also occurs to provide better packing.

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Structure of the Thiopeptide (Z)-Glyt-Gly-OBzl

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Abstract. *N*-[(*N*-Benzyloxycarbonyl)thioglycyl]glycine benzyl ester, $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$, $M_r = 372.4$, monoclinic, $P2_1$, $a = 9.76$ (1), $b = 10.01$ (2), $c = 20.68$ (3) Å, $\beta = 69.7$ (1)°, $V = 1894.3$ Å³, $Z = 4$, $D_m = 1.30$, D_x

$= 1.30 \text{ Mg m}^{-3}$, $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 1.69 \text{ mm}^{-1}$, $F(000) = 784$, $T = 293 \text{ K}$, $R = 0.048$ for 2958 reflections with $|F| \geq \sigma(F)$. The asymmetric unit contains two crystallographically independent peptide molecules in an extended form. The molecules are related to each other by a pseudo *a*-glide operation. They are arranged to form infinitely extended ribbons

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