1,4-Bishomo[6]prismane (Garudane): Molecular Structure and Strain Analysis of Reactions Potentially Leading to Prismanes

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The proposed structure of garudane (**1**), the face-to-face D_{2h} dimer of norbornadiene, has been confirmed by the X-ray analysis of a single crystal of the 1,3-bis(methoxycarbonyl) derivative (**2**), monoclinic, space group $C2/c$, $a = 16.570(6)$, $b = 8.073(4)$, $c = 12.151(4)$ Å, $\beta = 114.89(2)°$, final $R = 0.055$, $R_w = 0.070$. Detailed structural characteristics observed for (**2**) are compared with the isomeric D_{2d} dimer (isogarudane) (**3**). Compound (**1**) is calculated to be 44 kcal mol⁻¹ more strained than (**3**). The demethylenation procedure on (**1**)—and the 1,4-bis homo[7]prismane (**10**) of similar structure— as a potential synthetic route to [6]- and [7]-prismanes (**4**) and (**5**) has advantages over the intramolecular [2 + 2]-photocyclization of polycyclic dienes [*e.g.* (**12**) and (**13**)] and the pinacolic coupling of polycyclic diketones [*e.g.* (**14**)]. These are discussed on the basis of strain analysis.

A synthesis of the long-sought, elusive, face-to-face [2 + 2]-dimer of norbornadiene (**1**) (garudane), has recently been reported by two of us (S. P. and G. M.).[1,2] The structural novelty present in (**1**) and further exploration of its chemistry prompted us to an unambiguous confirmation of its 1,4-bishomo[6]prismane formulation. Towards this end, a single crystal X-ray analysis of a 1,3-bis(methoxycarbonyl) derivative (**2**), the penultimate intermediate in the synthetic sequence leading to (**1**), has been carried out. The detailed structure of (**2**) and comparisons of structure as well as strain aspects of (**1**) and (**2**) with one of the known [2 + 2] norbornadiene dimers, (**3**) (isogarudane or cyclo-octaquinone)[3] are reported here. This paper also discusses the implications of strain analysis in evaluating the synthetic strategy leading to our ultimate targets, [6]- and [7]-prismanes (**4**) and (**5**), starting with (**1**) and related molecules.

Results and Discussion

Molecular Structure of (**2**).—The results of X-ray analysis (see the Experimental) show that there are no unusual bond distances and angles in the observed structure of the heptacyclotetradecane (**2**) (Tables 1 and 2, and Figures 1 and 2). The cyclobutane ring C(3)–C(6)–C(3)*–C(6)*, carrying methoxycarbonyl groups, is slightly puckered, which indicates small repulsive interactions between 1,3-diaxial substituents.

A close look at the norbornane part reveals that the well-known, uneven bond distances and valence angles in the parent norbornane skeleton (**6**),[4] are retained in the garudane (**2**)

$$C(2)-C(3) \gg C(1)-C(7) > C(1)-C(2),$$

$$C(2)-C(1)-C(6) > C(2)-C(1)-C(7) \gg C(1)-C(7)-C(4),$$

(Table 3). This feature contrasts with isogarudane (**3**), wherein the structural feature peculiar to norbornane is slightly altered (Table 3). As noted by Hargittai,[5] the most notable alteration occurs in the C(2)–C(1)–C(6) angle, which is about 10° smaller in (**3**) compared with those in (**2**) and (**6**).

The subtle structural features of (**2**) and (**3**) may best be understood as a slight flattening in (**2**) and folding in (**3**) of the C_{2v} boat-shaped cyclohexane ring of the norbornane partial

(**1**) R = H
(**2**) R = CO₂Me

(**3**)

(**4**)

(**5**)
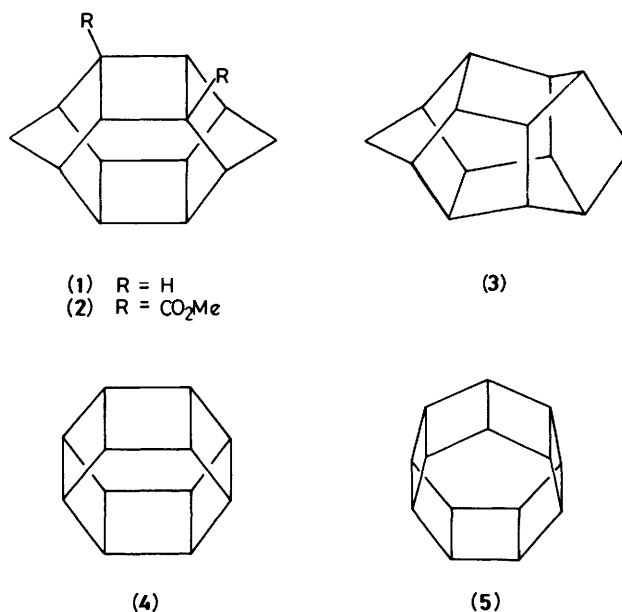
structure. The characteristic dihedral angle δ of the six-membered ring [71.6° for free (**6**) itself] is slightly decreased in (**2**) but slightly increased in (**3**) (Table 3). Small deformations of the norbornane moiety exert contrasting energetic consequences. As shown in Figure 3, where changes in MM2-steric energies are plotted against the deformation of isolated (**6**) along the C_{2v} 'reaction co-ordinate,' the gradient is smaller to the left of the energy minimum than to the right. Since the deformation to the left corresponds to a flattening motion and that to the right to a folding motion, the former should be more energetically efficient than the latter. We estimate that increased folding in the norbornane moieties of (**3**) raised the molecular strain by about 4 kcal mol⁻¹,† but flattening in the similar part of (**2**) did not affect the strain.

† 1 kcal = 4.184 kJ

Table 1. Bond distances of (2) in Å. Estimated standard deviations (e.s.d.s) in the least significant figure are given in parentheses.

O(1)–C(2)	1.196(4)	C(7)–C(8)	1.518(5)
O(2)–C(2)	1.316(3)	C(7)–C(9)*	1.553(5)
O(2)–C(1)	1.439(5)	C(1)–H(2)	0.86(6)
C(2)–C(3)	1.487(4)	C(1)–H(3)	0.86(8)
C(3)–C(4)	1.538(4)	C(1)–H(1)	0.92(5)
C(3)–C(6)	1.549(4)	C(4)–H(4)	0.97(3)
C(3)–C(6)*	1.563(4)	C(5)–H(5)	0.95(4)
C(4)–C(5)	1.522(5)	C(6)–H(6)	0.96(3)
C(4)–C(9)	1.545(4)	C(7)–H(7)	1.09(3)
C(5)–C(8)	1.551(5)	C(8)–H(8)	0.85(4)
C(5)–C(8)*	1.553(5)	C(9)–H(9)	1.01(4)
C(6)–C(7)	1.517(4)	C(9)–H(10)	1.04(4)

Table 2. Valence angles of (2) in degrees. E.s.d.s in the least significant figure are given in parentheses.

C(2)–O(2)–C(1)	117.3(3)	H(2)–C(1)–H(3)	97(5)
O(1)–C(2)–O(2)	122.7(3)	H(2)–C(1)–H(1)	99(4)
O(1)–C(2)–C(3)	126.0(3)	H(2)–C(1)–O(2)	117(4)
O(2)–C(2)–C(3)	111.3(3)	H(3)–C(1)–H(1)	121(5)
C(2)–C(3)–C(4)	112.4(2)	H(3)–C(1)–O(2)	116(5)
C(2)–C(3)–C(6)	117.0(2)	H(1)–C(1)–O(2)	105(3)
C(2)–C(3)–C(6)*	112.0(2)	H(4)–C(4)–C(5)	118(2)
C(4)–C(3)–C(6)*	102.8(2)	H(4)–C(4)–C(3)	115(2)
C(4)–C(3)–C(6)	120.6(2)	H(4)–C(4)–C(9)	110(2)
C(6)–C(3)–C(6)*	89.9(2)	H(5)–C(5)–C(4)	112(2)
C(5)–C(4)–C(3)	110.4(3)	H(5)–C(5)–C(8)	113(2)
C(5)–C(4)–C(9)	101.1(3)	H(5)–C(5)–C(8)*	114(2)
C(3)–C(4)–C(9)	99.7(2)	H(6)–C(6)–C(7)	114(1)
C(4)–C(5)–C(8)	121.5(3)	H(6)–C(6)–C(3)	112(2)
C(4)–C(5)–C(8)*	103.6(3)	H(6)–C(6)–C(3)*	111(2)
C(8)–C(5)–C(8)*	90.1(3)	H(7)–C(7)–C(6)	114(2)
C(7)–C(6)–C(3)*	104.7(2)	H(7)–C(7)–C(8)	115(2)
C(7)–C(6)–C(3)	121.4(2)	H(7)–C(7)–C(9)*	116(2)
C(3)–C(6)–C(3)*	90.0(2)	H(8)–C(8)–C(7)	116(2)
C(6)–C(7)–C(8)	110.4(2)	H(8)–C(8)–C(5)	110(2)
C(6)–C(7)–C(9)*	99.3(2)	H(8)–C(8)–C(5)*	112(2)
C(8)–C(7)–C(9)*	100.7(3)	H(9)–C(9)–H(10)	107(3)
C(7)–C(8)–C(5)	121.5(3)	H(9)–C(9)–C(4)	116(2)
C(7)–C(8)–C(5)*	104.0(3)	H(9)–C(9)–C(7)*	108(2)
C(5)–C(8)–C(5)*	89.9(3)	H(10)–C(9)–C(4)	117(2)
C(4)–C(9)–C(7)*	94.6(3)	H(10)–C(9)–C(7)*	113(2)

The molecules (1), (3), and (6) are quite similar, although the strain energies are greatly different. According to MM2 calculations (Table 4), (1) is 44 kcal mol^{-1} more strained than (3). If one subtracts twice the strain of (6) from the strain of (1), the remainder is 56 kcal mol^{-1}, which can be almost completely accounted for by the strain of two cyclobutane rings (26.95[3] or 26.5[6] kcal mol^{-1} per ring). A similar subtraction for (3) leaves 12.3 kcal mol^{-1} of strain. Further subtraction of 4 kcal mol^{-1}, due to the folding deformation mentioned above, leaves 8.3 kcal mol^{-1}, which should be due to four cyclopentane rings between the two norbornane partial structures. (The strain energy of isolated cyclopentane is estimated to be 6.2–7.1 kcal mol^{-1}.)[4,5]

Strain Considerations on the Synthetic Possibilities of Higher Prismanes from Garudane (1) and Related Intermediates.—The higher strain in (1) than (3) provides an advantage in further straining its structure towards [6]prismane.[7–10] The increase in the MM2-strain energy (ΔE_S) which accompanies replacement
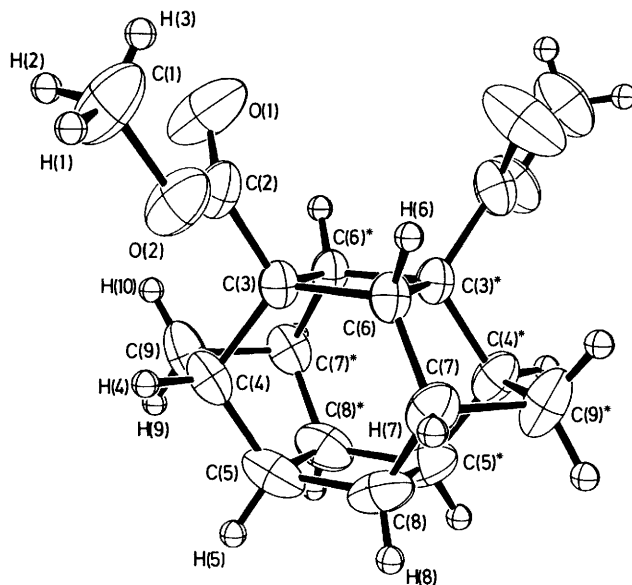
Figure 1. ORTEP drawing of the molecular structure of (2) as determined by X-ray analysis. The molecule is situated about a twofold crystallographic axis and therefore only half of the molecule is unique (*cf.* Figure 2).
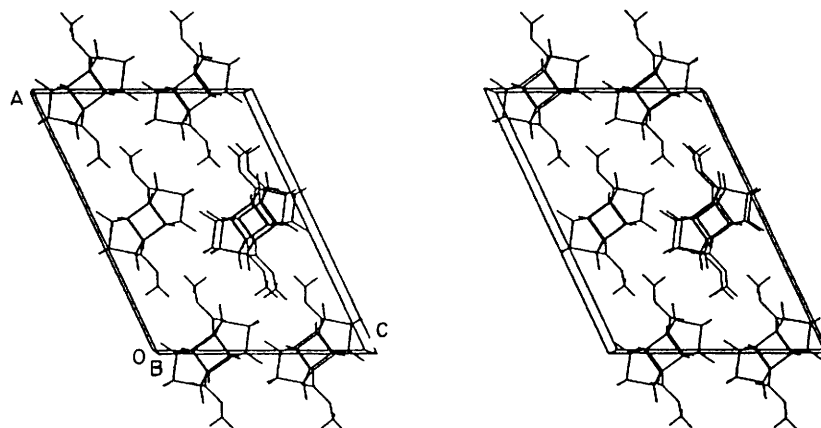
Figure 2. ORTEP stereo pair drawing of an unit cell of (2).

Table 3. Selected structural features in norbornane (6), garudane (1), 1,3-bis(methoxycarbonyl)garudane (2), and isogarudane (3).[a,b]

		ED[c]	MM2	MM2	X[d,e]	X[f]	ED[g]	MM2
		(6)	(6)	(1)	(2)	(3)	(3)	(3)
Bond length/Å	C(2)–C(3)	1.573(15)	1.541	1.558	1.558(7)	1.561(2)	1.586(4)	1.546
	C(1)–C(7)	1.546(24)	1.538	1.543	1.549(6)	1.523(5)	1.532(5)	1.531
	C(1)–C(2)	1.536(15)	1.542	1.530	1.524(10)	1.532(6)	1.553(4)	1.538
Valence angle/°	C(2)–C(1)–C(6)	109.0(1)	109.2	112.5	110.4(3)	100.1(3)	99.3(3)	100.7
	C(2)–C(1)–C(7)	102.0(1)	102.1	100.7	110.2(3)	104.2(2)	104.3(2)	104.4
	C(1)–C(7)–C(4)	94.3(1)	92.5	93.2	94.6(3)	94.6(1)	95.8(3)	93.3
δ/°[h]		71.6	71.4	69.9	69.5(3)	—	—	74.1
				27.9[i]	28.2(3)[i]			

[a] X = X-Ray, ED = Electron diffraction. [b] Atom numbers refer to (6). [c] L. Doms, L. Van den Enden, H. J. Geise, and C. Van Alsenoy, *J. Am. Chem. Soc.*, 1983, **105**, 158. [d] This work. [e] Average of the values at symmetrically equivalent positions given in Tables 1 and 2. [f] A derivative, ref. 3. [g] Ref. 5. [h] The extent of folding in a boat cyclohexane conformation (C_{2v}, endocyclic twist angles δ,0, −δ,δ,0, −δ) can be represented by the characteristic angle δ. In free boat cyclohexane, δ = 52.5 (MM2) or 51.9° (O. Ermer, P. M. Ivanov, and E. Ōsawa, *J. Comput. Chem.*, 1985, **6**, 401). For (3) δ is taken from the MM2-optimized structure. Subtle structural features in (1), (3), and (6) are well reproduced with MM2. [i] Pertains to the boat cyclohexane partial structure [C(1)–C(2)–C(6)–C(7)–C(11)–C(1)] involving the new bonds formed during dimerization.
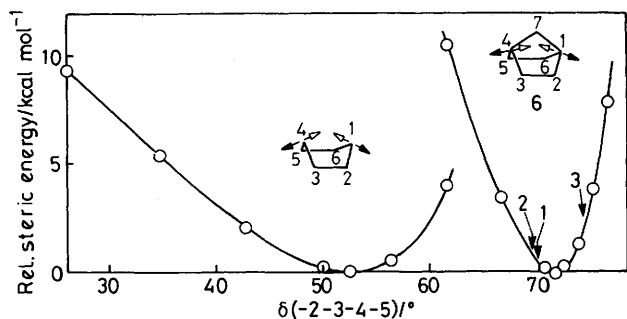
Figure 3. Variation of steric energy in the folding/unfolding (flattening) motions of bicyclo[2.2.1]heptane (6) and boat-shaped cyclohexane while keeping C_{2v} symmetry. Ordinates are MM2-minimized energy and abscissa characteristic dihedral angle δ in the six-membered ring. See footnote *h* of Table 3 for the definition of the characteristic dihedral angle of boat cyclohexane. Folding and flattening motions are indicated with the open and full arrows, respectively.

of a methylene group in (1) with a C–C bond is only about 30 kcal mol⁻¹ (Figure 4). It may be noted that this level of ΔE_S is considerably lower than the corresponding values calculated for the known[11] demethylenation of a bishomocubane (7) and a homocubane (8) (Figure 4). The same argument applies to a potential conversion of 1,4-bishomo[7]prismane (9) and seco-homo[7]prismane (10)[12] into (5) and seco[7]prismane (11), respectively (Figure 5). Note that the ΔE_S values which are expected to accompany the [2 + 2] photocyclization of juxtaposed dialkenes such as (12) and (13) leading to prismanes exceed 60 kcal mol⁻¹ [8,12] and such attempts have not been successful so far.

(12)   (13)
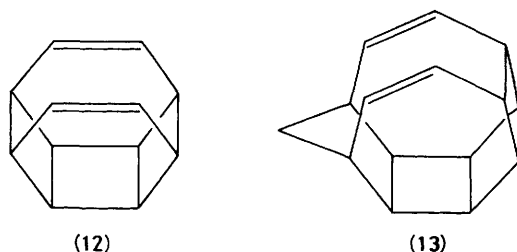
**Table 4.** MM2 energies (kcal mol⁻¹) of garudane (1), isogarudane (3), and norbornane (6).

		(1) D_{2h}	(3) D_{2d}	(6) C_{2v}
Steric energy	Stretch	2.30	1.44	0.80
	Bend	50.19	23.21	9.05
	St-Bd	−2.66	−1.28	−0.45
	Non-bonded	4.27	1.13	3.51
	Torsion	48.31	34.14	10.18
	Total	102.41	58.65	23.09
Strain energy		93.00	49.24	18.46
Heat of formation		54.39	10.62	−12.84

One of the key intermediates in the synthesis of (1) is the readily available hexacyclohexadecadione (14),[1] which appeared to be a potential precursor of 1,4-bishomo[7]prismane [(9)-diol, Figure 6]. We examined the possibility of (14) ⟶ (9)-diol conversion (*e.g.*, by intramolecular pinacolic coupling) in terms of our steric criteria,[8,12,13] namely the distance between carbonyl carbon atoms and the dihedral angle between the carbonyl planes of the starting diketones, in addition to ΔE_S of the hypothetical reaction. While the calculated distance between the carbonyl carbon atoms in (14) (2.80 Å) does not seem unusually large, the dihedral angle (119°) and ΔE_S (60 kcal mol⁻¹) values calculated for the conversion of (14) to (9)-diol exceed considerably the empirical thresholds of 50° and 55 kcal mol⁻¹, respectively,[9] and render this reaction highly unfavourable. In accordance with this prediction, attempts to effect this transformation experimentally under a variety of reaction conditions have been unsuccessful.

It is of some interest to seek the reason why the ΔE_S values calculated for the reactions, discussed above (type 1 reaction shown in Figure 7), are so much higher than those of the demethylenation reactions mentioned previously in Figure 4 and 5 (type 2 reaction in Figure 7). A close look at the optimized geometries of (10), (11), and (14), which contain structural elements for the type 1 reaction, has revealed that boat cyclohexane rings in these molecules are much more flattened than in the free state: the characteristic dihedral angles δ (see footnote *h* of Table 3) of (10), (11), and (14) are 32–36°,

(1) 93.00   124.97   (4) 156.32
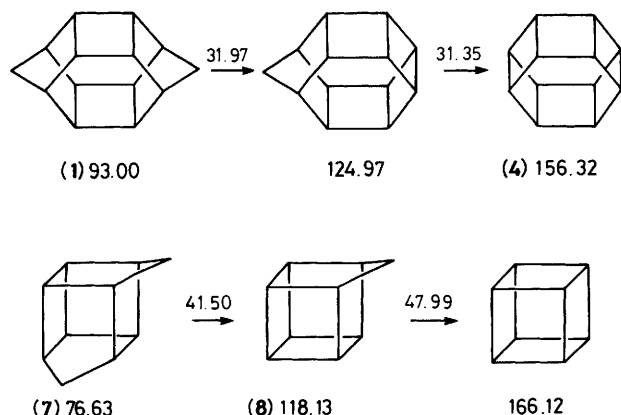
Figure 4. Strain energies (MM2, kcal mol^{-1}) of [4]- and [6]-prismane (4) and their mono- and bishomologues. Numbers above the arrow are 'strain increase' (ΔE_S) accompanied by the hypothetical reaction.

(7) 76.63   (8) 118.13   166.12

(9) 148.42   177.26   (5) 205.85

(10) 121.02   (11) 149.40
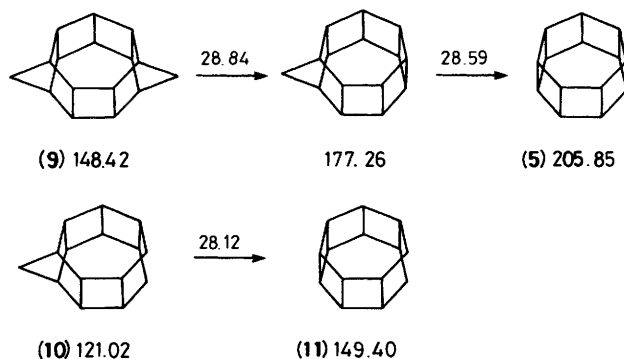
Figure 5. Strain energies (MM2, kcal mol^{-1}) of [7]- and nor[7]-prismane (5) and (11) and their mono- and bis-homologues. Numbers above the arrow are 'strain increase' (ΔE_S) accompanied by the hypothetical reaction.

(14)   (9)-diol
strain = 89.64   150.12 kcal
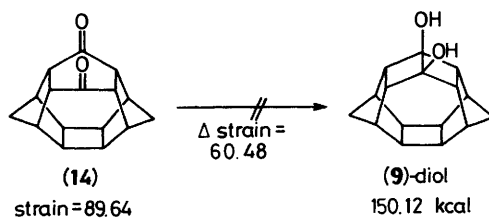
Figure 6. Strain increase (ΔE_S, kcal mol^{-1}) accompanied by intramolecular pinacolic coupling of polycyclic diketone (14) as calculated by MM2. Drawing represents the MMS-optimized structure.

considerably smaller than the value of 52° in the free-boat cyclohexane. In other words, the boat cyclohexane portions in these molecules can be extensively relaxed to absorb a considerable portion of the total molecular strain, whereas such relaxation is obviously energetically too costly for the nor-bornane moiety of the starting molecule in the type 2 reaction, as illustrated in Figure 3. As a consequence of better release of strain in the type 1 reactant (hence lower energy), the barrier of the reaction (ΔE_S) must be higher than that of the type 2 reaction.

One may reasonably conclude that in considering the various synthetic options open to highly catenated polycyclobutanes, it would be more advantageous to have a methylene bridge in the

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* Performed at the Molecular Structure Corporation

Figure 7. Two alternative synthetic routes (types 1 and 2) for building up catenated polycyclobutane units.

position at which a key cyclobutane forming carbon–carbon bond will be introduced in the advanced stages of the synthesis.[11,14]

Experimental

X-ray Analysis of (2).*—A colourless, block crystal of (2), m.p. 93–96 °C (pentane), dimensions *ca.* 0.30 × 0.35 × 0.40 mm, was mounted on a glass fibre. All measurements were made on a Rigaku AFC6R diffractometer with graphite mono-chromated Mo-K_α radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $43.45 < 2\theta < 49.94°$ corresponded to a monoclinic cell, $a = 16.570(6)$ Å, $b = 8.073(4)$ Å, $c = 12.151(14)$ Å, $\beta = 114.89(2)°$, $V = 1\,475(1)$ Å^3. For $Z = 4$ and $M = 300.35$ ($C_{18}O_4H_{20}$), the calculated density is 1.353 g cm^{-3}. Based on systematic absence of $hkl: h + k \neq 2n$ and $h0l: l \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $C2/c$. The data were collected at a temperature of 25 ± 1 °C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0°. Scans of $(1.42 + 0.30 \tan \theta)°$ were made at a speed of 16.0° min^{-1} (in ω). The weak reflections $[I < 10.0\sigma$ $(I)]$ were re-scanned (maximum of 2 re-scans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 40 cm.

Of 1 461 reflections which were collected, 1 408 were unique ($R_{int} = 0.014$). Intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo-K_α is 1.0 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 871 observed reflections $[I > 3.00\sigma (I)]$ and 140 variable parameters and converged (largest parameter shift was 0.11 times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma\|F_o\| - |F_c\|/\Sigma|F_o| = 0.055$, $R_\omega = [(\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)]^{1/2} = 0.070$. The standard deviation of an observation of unit weight (goodness of fit) was 2.02. The final fractional co-ordinates are given in Table 5.† The weighting scheme was based on counting

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† Non-hydrogen atom co-ordinates, thermal parameters, and tables of least-squares planes have been deposited at the Cambridge Crystallographic Data Centre. For details see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2* (1989), in the January issue.

Table 5. Fractional co-ordinates of crystallographically unique atoms of (2).

Atom	x	y	z
O(1)	0.379 8(2)	0.161 9(4)	0.602 0(3)
O(2)	0.308 0(1)	0.041 4(3)	0.697 3(2)
C(1)	0.248 5(4)	0.180 7(8)	0.670 1(5)
C(2)	0.370 7(2)	0.046 9(4)	0.657 8(3)
C(3)	0.427 7(2)	−0.103 5(3)	0.694 3(2)
C(4)	0.377 4(2)	−0.260 5(4)	0.629 8(3)
C(5)	0.428 0(2)	−0.414 7(4)	0.694 5(3)
C(6)	0.489 2(2)	−0.105 5(4)	0.833 3(2)
C(7)	0.499 8(2)	−0.260 0(4)	0.909 2(3)
C(8)	0.488 5(2)	−0.414 3(4)	0.832 6(3)
C(9)	0.397 6(2)	−0.257 9(6)	0.516 8(3)

statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\Sigma\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.33 and -0.27 e Å^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion effects were included in F_{calc};[17] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[18] All calculations were performed using the program TEXSAN.[19] Stereo pair drawings (Figures 1 and 2) were prepared with the program ORTEP.[20] Cyclobutane rings are practically planar: the distances from the least-squares plane are -0.0073 Å for C(3) and C(3)*, and 0.0086 Å for C(6) and C(6)*.

Computation.—Program MMP2(85)-PC was obtained from $QCPE$,[21] adopted to NECPC 9 801, and used throughout this work.

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