Hexacyclo[9.9.0.0²,⁹.0³,⁷.0¹²,¹⁹.0¹³,¹⁷]icosa-3(7),13(17)-diene-4,14-dione, an All-*cis* Polyquinane Derivative

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Abstract. $C_{20}H_{22}O_2$, $M_r = 294.38$, monoclinic, $a = 12.563$ (3), $b = 13.419$ (1), $c = 8.984$ (2) Å, $\beta = 93.03$ (1)°, $V = 1512.36$ Å³, $Z = 4$, $D_c = 1.29$ g cm⁻³, $F(000) = 632$; space group $P2_1/c$ from systematic absences; $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$; λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.45$ cm⁻¹. Full-matrix refinement using 2272 observed reflexions lowered R to 0.043. The molecule has approximate non-crystallographic twofold symmetry and its dimensions show that it is a possible precursor for dodecahedrane synthesis.

Introduction. In a previous communication (McKervey, Vibuljan, Ferguson & Siew, 1981) on dodecahedrane (1) synthesis (Eaton, 1979; Paquette, Balogh, Usha, Kountz & Christoph, 1981) we described the construction and X-ray analysis of a potential precursor having the all-*cis* hexaquinane structure (2); the molecule has an 'opened-out' conformation resulting from severe intramolecular overcrowding, particularly between the carbonyl groups and the methylene H atoms at C(7) and C(7′). In considering ways of reducing the intramolecular overcrowding and thereby reducing the distances between atoms C(3) and C(3′) in the dione (2), we have examined the diene-dione (3), the synthetic precursor to (2); this was synthesized as described previously (McKervey *et al.*, 1981).
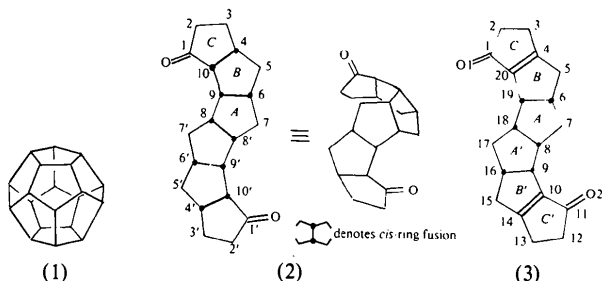
A small crystal of dimensions 0.50 × 0.25 × 0.25 mm was used in the X-ray analysis. Unit-cell constants

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and intensity data were determined using an Enraf–Nonius computer-controlled CAD-4 diffractometer. For the cell-dimension determination, the setting angles of 25 reflections with θ near 15° were used in a least-squares refinement. During data collection three well separated reflections were monitored at regular intervals and showed no reduction in intensity. The intensities of 2974 reflections with $2 < \theta < 25°$ were measured by the $\theta/2\theta$ scan technique. The 2272 reflections with $I > 3\sigma(I)$ were labelled 'observed' and used, after correction for Lorentz and polarization factors, in the determination and refinement of the structure.

Table 1. *Final fractional coordinates* (×10⁴) *and isotropic thermal parameters* (Å² ×10³) *with standard deviations in parentheses*

	x	y	z	$\bar{U}$
O(1)	5029 (1)	2160 (1)	6408 (2)	73 (1)
O(2)	10148 (1)	−1708 (1)	8111 (2)	70 (1)
C(1)	5454 (1)	1702 (1)	5428 (2)	42 (1)
C(2)	4874 (1)	1250 (1)	4068 (2)	43 (1)
C(3)	5731 (1)	756 (1)	3157 (2)	42 (1)
C(4)	6734 (1)	962 (1)	4088 (2)	34 (1)
C(5)	7883 (1)	730 (1)	3895 (2)	41 (1)
C(6)	8430 (1)	1070 (1)	5395 (2)	38 (1)
C(7)	8730 (1)	229 (1)	6483 (2)	40 (1)
C(8)	8684 (1)	694 (1)	8037 (2)	38 (1)
C(9)	8498 (1)	−12 (1)	9358 (2)	38 (1)
C(10)	8505 (1)	−1122 (1)	9076 (2)	38 (1)
C(11)	9260 (1)	−1850 (1)	8531 (2)	47 (1)
C(12)	8714 (1)	−2866 (1)	8585 (3)	58 (1)
C(13)	7622 (1)	−2682 (1)	9225 (3)	53 (1)
C(14)	7615 (1)	−1578 (1)	9447 (2)	40 (1)
C(15)	6827 (1)	−882 (1)	10063 (2)	48 (1)
C(16)	7316 (1)	156 (1)	9776 (2)	41 (1)
C(17)	6806 (1)	706 (1)	8436 (2)	40 (1)
C(18)	7688 (1)	1368 (1)	7881 (2)	38 (1)
C(19)	7598 (1)	1702 (1)	6229 (2)	36 (2)
C(20)	6584 (1)	1475 (1)	5331 (2)	34 (1)

$\bar{U}$ is the average of the three eigenvalues of each anisotropic vibration tensor.

Table 2. *Interatomic distances* (Å) *and angles* (°)

O(1)–C(1)	1·221 (2)	C(9)–C(10)	1·510 (2)
O(2)–C(11)	1·211 (2)	C(9)–C(16)	1·567 (2)
C(1)–C(2)	1·516 (2)	C(10)–C(11)	1·465 (2)
C(1)–C(20)	1·458 (2)	C(10)–C(14)	1·332 (2)
C(2)–C(3)	1·537 (2)	C(11)–C(12)	1·527 (2)
C(3)–C(4)	1·501 (2)	C(12)–C(13)	1·535 (2)
C(4)–C(5)	1·496 (2)	C(13)–C(14)	1·495 (2)
C(4)–C(20)	1·333 (2)	C(14)–C(15)	1·489 (2)
C(5)–C(6)	1·549 (2)	C(15)–C(16)	1·550 (2)
C(6)–C(7)	1·527 (2)	C(16)–C(17)	1·525 (2)
C(6)–C(19)	1·567 (2)	C(17)–C(18)	1·525 (2)
C(7)–C(8)	1·533 (2)	C(18)–C(19)	1·548 (2)
C(8)–C(9)	1·547 (2)	C(19)–C(20)	1·503 (2)
C(8)–C(18)	1·544 (2)		

O(1)–C(1)–C(2)	125·0 (1)	O(2)–C(11)–C(10)	128·5 (1)
O(1)–C(1)–C(20)	127·8 (2)	O(2)–C(11)–C(12)	124·9 (1)
C(2)–C(1)–C(20)	107·3 (1)	C(10)–C(11)–C(12)	106·5 (1)
C(1)–C(2)–C(3)	106·3 (1)	C(11)–C(12)–C(13)	106·3 (1)
C(2)–C(3)–C(4)	102·4 (1)	C(12)–C(13)–C(14)	102·8 (1)
C(3)–C(4)–C(5)	133·1 (1)	C(10)–C(14)–C(13)	114·2 (1)
C(3)–C(4)–C(20)	114·2 (1)	C(13)–C(14)–C(15)	132·8 (1)
C(5)–C(4)–C(20)	112·6 (1)	C(10)–C(14)–C(15)	112·9 (1)
C(4)–C(5)–C(6)	103·0 (1)	C(14)–C(15)–C(16)	102·9 (1)
C(5)–C(6)–C(7)	115·0 (1)	C(9)–C(16)–C(15)	107·4 (1)
C(5)–C(6)–C(19)	107·4 (1)	C(9)–C(16)–C(17)	104·2 (1)
C(7)–C(6)–C(19)	104·0 (1)	C(15)–C(16)–C(17)	114·3 (1)
C(6)–C(7)–C(8)	105·2 (1)	C(16)–C(17)–C(18)	104·9 (1)
C(7)–C(8)–C(9)	117·6 (1)	C(8)–C(18)–C(17)	103·2 (1)
C(7)–C(8)–C(18)	103·0 (1)	C(8)–C(18)–C(19)	105·9 (1)
C(9)–C(8)–C(18)	105·9 (1)	C(17)–C(18)–C(19)	117·7 (1)
C(8)–C(9)–C(10)	118·3 (1)	C(6)–C(19)–C(18)	106·6 (1)
C(8)–C(9)–C(16)	106·2 (1)	C(6)–C(19)–C(20)	101·6 (1)
C(10)–C(9)–C(16)	101·3 (1)	C(18)–C(19)–C(20)	118·2 (1)
C(9)–C(10)–C(11)	136·4 (1)	C(1)–C(20)–C(4)	109·8 (1)
C(9)–C(10)–C(14)	113·5 (1)	C(1)–C(20)–C(19)	136·5 (1)
C(11)–C(10)–C(14)	110·1 (1)	C(4)–C(20)–C(19)	113·6 (1)

The structure was determined by direct methods using the *SHELX* program (Sheldrick, 1976). The first *E* map calculated with *E*'s >1·2 revealed all 22 non-H atoms. Four cycles of full-matrix isotropic refinement reduced *R* to 0·136 and a subsequent difference map revealed positions for all 22 protons. These were then allowed for in idealized positions (C–H 0·95 Å) and only an overall isotropic temperature factor was refined for H atoms in subsequent refinement. After seven further rounds of full-matrix calculations, with the non-H atoms allowed anisotropic thermal vibration, the refinement had completely converged with $R = 0·043$ and $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0·056$. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2 F + 0·003F^2)$, and scattering factors were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). A final difference map was free of any significant features. Final fractional coordinates are given in Table 1 and details of molecular geometry are in Table 2.*

Discussion. The crystal structure of the diene-dione (3) (Fig. 1) contains discrete molecules (Fig. 2) separated by normal van der Waals distances. Although no crystallographic symmetry is required for (3) by the space group it conforms to twofold symmetry within the accuracy of the analysis. The dione (2) has crystallographic twofold symmetry and comparison of data for (2) with those of (3) shows that the presence of two olefinic bonds in (3) has a major effect on the conformation of the *entire* molecule. In particular, (3) has a *less* opened out conformation than (2), although quite the opposite might have been expected to occur on replacing *cis* CH–CH groups by planar olefin moieties. Thus, whereas distances in (3) of the C(7)···O(2) type [C(7)···O(2) 3·434 and C(17)···O(1) 3·418 (2) Å] and the C(7)···C(11) type [C(7)···C(11) 3·389 and C(17)···C(1) 3·390 (2) Å] are significantly *longer* than the corresponding distances in (2) [C(7)···O(2) 3·144 (3), C(7)···C(11) 3·074 (3) Å], the critical transannular distances in (3) [C(3)···C(13) 7·436 (2) Å, a single bond in (1), and C(3)···C(12) 7·714 (2) Å] are significantly *shorter* than the corresponding distances in (2) [8·422 (3) and 7·996 (3) Å respectively]. These reductions are accompanied by differences in ring conformations between (2) and (3). In (2), the unique *A* ring has a C(8) envelope conformation whereas in (3) rings *A* and *A'* have a twist conformation intermediate between a C(7) [or C(17)] and C(8) [or C(18)] envelope. Ring *B* in (2) is a C(5) *endo*-envelope, whereas the *B* and *B'* rings in (3) are distorted from planarity towards a C(6) [or C(16)] *endo*-envelope conformation. The C(3) *exo*-envelope conformation found for ring *C* in (2) contrasts with the essentially planar *C* and *C'* rings in (3). The exocyclic angles at C(9) and C(19) in (3) [118·3 and 118·2 (1)°], while being much larger than tetrahedral, are considerably smaller than that found in (2)
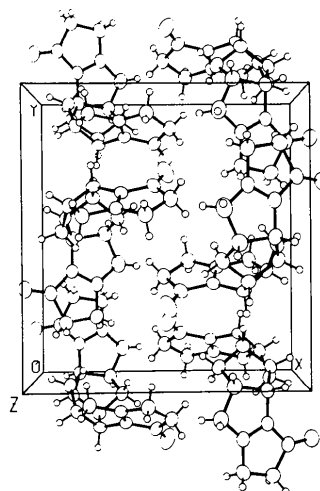

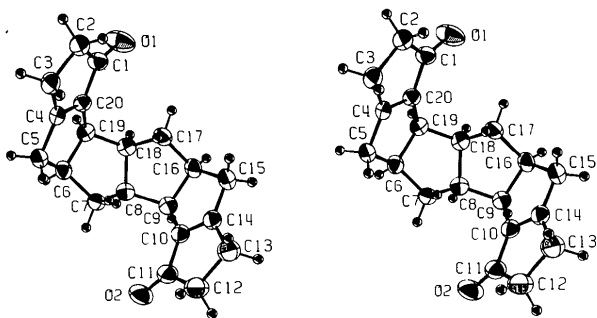Fig. 1. View of the crystal structure of (3).

Fig. 2. Stereoview of a molecule of (3) showing the crystallographic numbering scheme.

[123·4 (2)°]. This set of structural changes, resulting in a *less* opened-out structure for (3) compared with (2), provides a better precursor for eventual closure to the dodecahedrane nucleus. Further synthetic work on (3) is in progress.

The bond lengths in (3), Table 2, are for the most part unexceptional except for the distances C(6)—C(19)

and C(9)—C(16) [both 1·567 (2) Å] which are much longer than expected for normal $C(sp^3)$—$C(sp^3)$ bonds and are considered to be a result of strain in the molecule.

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SHORT COMMUNICATION

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Correlations in multipole refinements of ethylene.

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Abstract

Multipole refinements of C_2H_4 have shown that the positional and thermal parameters of C depend on the radial distribution functions adopted for the dipole and monopole. Values obtained from high-order refinements are approached best for monopole and dipole radial functions derived from SCF (Clementi) wavefunctions, or for a single exponential function $r^n \exp(-\alpha r)$ with $n = 2$ for the dipole.

Introduction

In accurate electron density studies by X-ray diffraction, often the observed one-electron density distribution is given with respect to a reference model consisting of a superposition of non-bonded vibrating atoms: the IAM model. The deformation density

$$D(\mathbf{r}) = K\rho(\text{obs};\mathbf{r}) - \rho(\text{IAM};\mathbf{r}) \qquad (1)$$

gives, apart from random errors, a correct picture of the deviations of the observed density from the reference model,

if the scale factor K and the positions and thermal parameters of the IAM atoms are correct. In principle IAM parameters can be determined by neutron diffraction, but in practice difficulties often arise due to a difference in systematic errors for the two experiments (Scheringer, Kutoglu & Mullen, 1978), or because suitable crystals are not available for the neutron diffraction work. In such cases attempts can be made to determine the IAM parameters and K from multipole refinements.

Multipole refinements on C_2H_4

For the volatile compound C_2H_4 no suitable crystals for neutron diffraction were available. Therefore van Nes & Vos (1979) have carried out two types of multipole refinements with the program *VALRAY* (Stewart, 1974) to obtain the IAM parameters. In both refinements the radial function for the carbon core was deduced from the Clementi (1965) wavefunction for the K shell. The H-atom positions were constrained relative to those of the adjacent C atoms on the basis of the molecular geometry of gaseous C_2H_4 (Duncan,