

separation between reactive C atoms of 4.25 Å, between C2...C2 (at $-x$, $-y$, $1-z$). Nevertheless this does not afford a mechanism for polymerization since the shortest approach between reactive C atoms in *different* pairings is 5.61 Å, between C2'...C2 (at x , $\frac{1}{2}-y$, $-\frac{1}{2}+z$). This is both too long and chemically incompatible for an infinite reaction which would here require alternating contacts of type C2...C2 and C2'...C2'. The shortest C2'...C2' approach between different pairs of molecules is at 6.43 Å.

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(E)-1-Cyano-2,6-dimethoxy-3-fulvenyl Acetate

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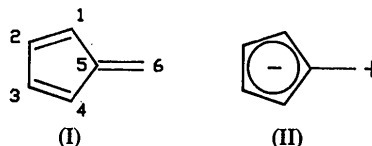
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Abstract. (E)-1-Cyano-2,6-dimethoxy-3-fulvenyl acetate, C₁₁H₁₁NO₄, $M_r = 221.21$, monoclinic, $P2_1$, $a = 4.079$ (7), $b = 8.096$ (2), $c = 16.518$ (5) Å, $\beta = 95.07$ (6)°, $V = 543$ (1) Å³, $Z = 2$, $D_x = 1.352$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.112$ mm⁻¹, $F(000) = 232$, room temperature, $R = 0.044$ for 631 observed reflections. In contrast to other fulvenes with electron-donor substituents on the exocyclic C atom (C6), which have intermediate single-double bond lengths, the title compound shows a clear double-bond fixation in the fulvenic system. The dipolar canonical forms do not contribute significantly to the structure description.

Introduction. The fulvenes are an interesting class of compounds with properties that lie between those of polyenes and aromatic compounds such as benzene. Their behaviour depends on the contribution of each canonical form to the real structure. If form (II) is predominant the fulvene has aromatic character because of the presence of 6π electrons delocalized in the ring; conversely, if form (I) is predominant the molecule exhibits polyenic character. The contribution of each canonical form is strongly determined by the substituents. The structures of fulvenes have

been analyzed by means of different physical and chemical methods, but whenever X-ray diffraction is possible it is preferred. Thus it has been shown that alkyl and aryl fulvenes are basically polyenic like fulvene (Norman & Post, 1961; Mano, Takusagawa, Hinamoto & Kushi, 1973), whereas a large number of 6-heterosubstituted fulvenes show aromatic character (Ammon, 1974; Ammon & Wheeler, 1975; Ammon & Erhardt, 1980; Böhme & Burzlaff, 1974). Other fulvenes have been described that have extended non-aromatic delocalization showing special features (Ferguson, Marsh, Restivo & Lloyd, 1975; Ficini, Revial & Jeannin, 1981; Fuess & Lindner, 1975; Bruce, Walton, Williams, Hall, Skelton & White, 1982). Recently our group has designed a synthesis for new highly functionalized fulvenes (Victory, Alvarez-Larena, Barbera, Batllori, Borrell & Córdoba, 1989). We present here the X-ray structure determination of the title compound in the context of a general study of the nature of these fulvenes.



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Experimental. Pale-yellow prismatic crystals grown from an ethyl acetate/hexane solution. A suitable single crystal ($0.05 \times 0.1 \times 1$ mm) was mounted on an Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. The cell parameters were determined from a least-squares fit to 25 reflections ($11 < 2\theta < 28^\circ$). The space group was uniquely determined from the observed extinctions. 1020 reflections were measured with an $\omega/2\theta$ scan, 631 with $I \geq 2.5\sigma(I)$ used in subsequent refinement; $\theta_{\max} = 25^\circ$. Three reflections monitored every 50 measurements; no significant change in intensity. Lorentz and polarization corrections were applied, but no absorption or extinction corrections were made. Index range: $h -4$ to 4 , $k 0$ to 9 , $l 0$ to 19 . The structure was solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), all non-H atoms were located from an E map prepared using the phase set with the highest figure of merit. The refinement was performed by full-matrix least squares on F using *SHELX* (Sheldrick, 1976). H-atom positions were calculated riding on the adjacent C atoms assuming C—H = 1.08 \AA , and refined with an overall isotropic temperature factor. Final $R = 0.044$, $wR = 0.044$, $w = 3.09/[\sigma^2(F) + 1.1 \times 10^{-4}F^2]$; maximum shift/e.s.d. = 0.04 ; max. and min. heights in final difference Fourier synthesis 0.15 and $-0.15 e \text{ \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Digital VAX 8800.

Discussion. Atomic parameters and geometrical data are given in Tables 1* and 2. The molecular structure with the atom numbering is presented in Fig. 1. Bond distances are very similar to those of 6,6-dimethylfulvene (Norman & Post, 1961), which is considered a completely polyolefinic structure; the greatest difference is 0.03 \AA in the bond C1—C5. Fixation of double bonds definitely occurs in the title compound. This result contrasts with those for 6-heterosubstituted fulvenes (described in the literature cited in the *Introduction*), which exhibit a greater delocalization. This unexpected situation can be attributed to special features of the substituents present on the fulvenic ring. Related to this fact, it is noteworthy that the C1—C7 and C1—C2 bond distances are, respectively, shorter and longer than those found in compounds having the C=C—CN substructure (Fukuyama & Kuchitsu, 1970; Quast,

Table 1. Final fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
C1	4907 (16)	-1093 (10)	2946 (3)	4.03
C2	6105 (15)	-1334 (11)	2204 (4)	3.90
C3	5686 (15)	154 (0)	1744 (3)	4.21
C4	4238 (15)	1326 (12)	2174 (4)	4.61
C5	3655 (16)	611 (11)	2949 (4)	4.17
C6	2281 (16)	1302 (11)	3570 (4)	4.64
C7	4817 (16)	-2144 (12)	3619 (4)	4.25
N8	4648 (16)	-2973 (11)	4186 (3)	6.13
O9	1196 (12)	2858 (10)	3538 (3)	5.60
O10	-304 (19)	3470 (11)	4251 (4)	5.86
O11	7544 (12)	-2637 (10)	1870 (2)	5.16
O12	7895 (21)	-4142 (11)	2346 (4)	5.38
O13	6750 (12)	139 (9)	969 (2)	5.39
O14	7310 (15)	1594 (13)	558 (4)	4.45
O15	6878 (16)	2908 (11)	860 (3)	8.06
O16	8320 (20)	1254 (12)	-250 (4)	6.47

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

C2—C1	1.374 (9)	C6—C5	1.333 (10)
C5—C1	1.471 (12)	O9—C6	1.335 (12)
C7—C1	1.403 (10)	N8—C7	1.159 (10)
C3—C2	1.426 (9)	C10—O9	1.461 (9)
O11—C2	1.348 (11)	C12—O11	1.450 (11)
C4—C3	1.352 (9)	C14—O13	1.389 (12)
O13—C3	1.388 (6)	O15—C14	1.195 (13)
C5—C4	1.444 (8)	C16—C14	1.457 (10)
C5—C1—C2	106.7 (5)	C6—C5—C1	124.4 (6)
C7—C1—C2	131.1 (7)	C6—C5—C4	128.8 (7)
C7—C1—C5	122.2 (6)	O9—C6—C5	121.8 (6)
C3—C2—C1	108.6 (5)	N8—C7—C1	177.3 (8)
O11—C2—C1	132.6 (7)	C10—O9—C6	116.8 (6)
O11—C2—C3	118.7 (5)	C12—O11—C2	117.5 (5)
C4—C3—C2	110.5 (3)	C14—O13—C3	121.5 (5)
O13—C3—C2	116.8 (4)	O15—C14—O13	121.0 (6)
O13—C3—C4	132.7 (3)	C16—C14—O13	111.1 (8)
C5—C4—C3	107.4 (6)	C16—C14—O15	127.9 (9)
C4—C5—C1	106.8 (6)		

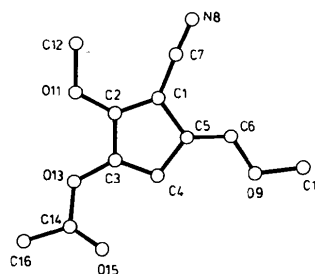


Fig. 1. View of the molecule with the atom-numbering scheme.

Görlach, Peters, Peters, Schnering, Jackman, Ibar & Freyer, 1986; Bryce, Reynolds, Hanson & Vernon, 1981) pointing to the presence of a push-pull olefin (MeO—C1=C2—CN) previously suspected on spectroscopic grounds (^{13}C NMR chemical shifts and IR stretching frequencies).

The methoxy group on C6 is situated in a *trans* position confirming the previous assignment based

* Lists of structure amplitudes, H-atom parameters, deviations from the fulvenic mean plane, anisotropic thermal parameters, and complete molecular geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51989 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

on ^1H NMR data. The fulvenic skeleton is planar. The cyano and methoxy groups are coplanar with the ring, while the acetoxy group deviates from it. The angle between the mean planes defined by the six fulvenic C atoms and the acetoxy group is $18.6 (3)^\circ$.

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Structure of an Open-Ended Cage Compound

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Abstract. 11-Oxo-8-propionyloxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-9-carboxylic acid (3a), $\text{C}_{15}\text{H}_{16}\text{O}_5$, $M_r = 276.29$, monoclinic, $P2_1/c$, $a = 7.610 (1)$, $b = 7.972 (1)$, $c = 21.329 (2) \text{ \AA}$, $\beta = 93.94 (1)^\circ$, $V = 1291.1 (2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.421 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.00 \text{ cm}^{-1}$, $F(000) = 584$, $T = 299 \text{ K}$, $R = 0.0427$ for 1437 independent reflections. The compound is composed of a norbornane moiety (two fused five-membered rings) fused along each side to five-membered rings which are joined to form a four-membered ring. The molecule is a cage with one side open. The two C atoms of the open end contain a ketone moiety and a planar *endo*-ester side chain. One end of the norbornane moiety, $1.573 (3) \text{ \AA}$, is significantly longer than all other

bonds in the structure. The four-membered ring has distances ranging from $1.542 (3)$ to $1.557 (3) \text{ \AA}$ and is planar, r.m.s.d. $\approx 0.002 \text{ \AA}$. The two C atoms at the open end of the cage are separated by $2.665 (3) \text{ \AA}$ with the carbonyl C atom slightly pyramidalized and lying out of the plane of the other three atoms by $0.051 (3) \text{ \AA}$. A hydrogen bond is formed between the acid group of one molecule and the keto of an adjacent molecule.

Introduction. The title reaction was studied as part of a program concerned with the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (Marchand, 1989). The starting material for this study (2) was synthesized by sodium borohydride reduction of the corresponding ketone, (1) (Scheme 1). The synthesis and structure of (1) have been reported previously (Watson, Nagl, Marchand, Reddy & Reddy, 1989). Based upon the

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