Structure and Bonding of 4,4-Dicyano-2,3-diphenyltriafulvene

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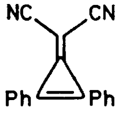
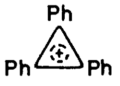
The crystals of the title compound are monoclinic, $C2/c$, with a = 14.31(1), b = 10.100(8), c = 9.607(8) Å, β = 106.57(6)°, and Z = 4. Least-squares refinement, based on 640 independent reflections, converged at R 0.043. The molecules possess crystallographic C_2 symmetry, with slight deviations from planarity. A simple electronic scheme, based on the Walsh model and a HMO calculation, for this and other similar cyclopropyl compounds, is proposed to rationalize the bond length values. This model also suggests that the high value of the dipole moment in this compound may be due to a partial delocalization of the electron density charge over the ring.

SMALL ring molecules have recently been used in ring opening reactions by nucleophilic attack of metal complexes, such as $Pt(PPh_3)_2$. The structure of the reaction product between 4,4-dicyano-2,3-diphenyltriafulvene (I), and $Pt(PPh_3)_2$ has been recently reported [1] and hence we found it of interest to establish the geometry of (I). Furthermore some years ago Agranat *et al.*[2] proposed a significant delocalization on the $C{=}(CN)_2$ portion of the molecule to explain the high value of the dipole moment (7.89 D in dioxan at 30 °C). Therefore detailed knowledge of the geometry of (I) should be useful to support this suggestion.

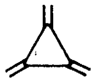


(I)



(II)

(III)



(IV)

EXPERIMENTAL

Crystal Data.—$C_{18}H_{10}N_2$, M = 254.3. Monoclinic, a = 14.31(1), b = 10.100(8), c = 9.607(8) Å, β = 106.57(3)°, U = 1 330.8 Å^3, D_c = 1.27 g cm^{-3}, Z = 4, D_m = 1.25 (by flotation), μ(Mo-K_α) = 0.82 cm^{-1}. Space group $C2/c$ (from structure determination).

Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line, automated, single-crystal diffractometer.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation for a maximum 2θ angle of 50°. Reflections with $I < 3\sigma(I)$ were rejected and the remainder corrected for Lorentz-polarization factors. A total of 640 independent reflections was used in the subsequent calculations. No absorption correction was applied (μR 0.02).

Structure Determination.—The structure was solved by a trial method since the crystal data and the expected shape of the molecule strongly suggested that each molecule should lie on the C_2 crystallographic axis. Furthermore the very strong -402 reflection suggested the tentative orientation of the molecule, assumed to be nearly planar. Thus a series of structure factor calculations by shifting the whole molecule (at intervals of y = 0.05, using 300 reflections) along the C_2 axis allowed the determination of the approximate values of the y co-ordinates. Subsequent isotropic refinement converged at R 0.14. After an anisotropic refinement, all hydrogen atom positions were obtained from the subsequent difference-Fourier map. The final anisotropic refinement, including the fixed contribution of hydrogen atoms (B 5 Å^2), gave R 0.043. The function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$ and the final weighting scheme: $w = 1/(A + |F_o| + B|F_o|^2)$ with A 5 and B 0.003 2 chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\theta/\lambda)$.

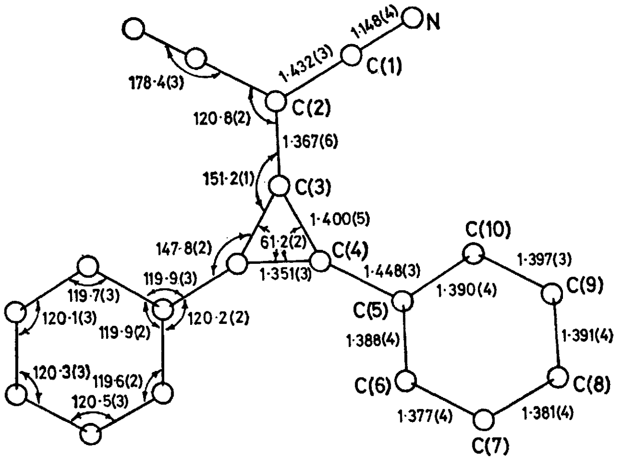


FIGURE 1 A view of (I) together with the numbering scheme. Bond lengths and angles are given with the estimated standard deviations in parentheses

Atomic parameters are listed in Table 1, together with their estimated standard deviations. The numbering scheme of the atoms is shown in Figure 1. Atomic scattering factors were those of ref. 3. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22404 (4 pp.).†

Calculations.—All calculations were carried out on a CDC 6200 computer using programs written by Immirzi [4] and Albano *et al.*[5]

RESULTS AND DISCUSSION

Description of the Structure.—The molecular structure of (I) is shown in Figure 1 together with bond lengths and angles. The molecule has exact C_2 crystallographic

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

symmetry and deviates from C_{2v} symmetry because of the slight rotation (5.8°) of its phenyl groups out of the plane of the remaining atoms which are coplanar within ± 0.014 Å. If the cyano groups are excluded, the whole geometry approaches that found for diphenylcyclopropenethione,[6] suggesting that both $C(CN)_2$ and S groups do not exert a significant influence at this level. In fact in diphenylcyclopropenethione the C(3)–C(4) and C(4)–C(4′) distances are 1.403 and 1.338 Å, whereas the endocyclic angle at C(3) is 61.5° and the exocyclic angles at C(3) are 146.4 and 152.0°, respectively. Data reported[7] for diphenylcyclopropenone are of too low accuracy to be taken into account. In order to discuss the bond nature in (I) it is of interest to compare its bond lengths with those of analogous compounds containing three-membered rings such as *sym*-triphenylcyclopropenium ion[8] (II), cyclopropene[9] (III), and trimethylenecyclopropene[10] (IV). Table 2 gives the values of the C–C bond lengths which are all equal in (II) and (IV), 1.373(10) (mean) and 1.453(20) Å respectively. On the other hand one short bond length [1.305(3) Å] is evident in (III) compared with the other two of 1.521(2) Å, suggesting the existence of a localized double bond. Thus endocyclic bond lengths in (I) [two C–C distances of 1.400(5) Å and one of 1.351(3) Å] suggest an electronic situation intermediate between the complete delocalization in (II) and the nearly complete localization in (III).

TABLE 1

Atomic positional parameters ($\times 10^4$) of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
N	3 952(2)	6 389(3)	276(3)
C(1)	4 422(2)	5 835(3)	1 275(3)
C(2)	5 000(0)	5 110(4)	2 500(0)
C(3)	5 000(0)	3 757(4)	2 500(0)
C(4)	4 682(2)	2 543(3)	1 828(2)
C(5)	4 070(2)	1 850(3)	580(2)
C(6)	3 983(2)	480(3)	605(3)
C(7)	3 368(2)	−168(3)	−580(3)
C(8)	2 860(2)	533(3)	−1 789(3)
C(9)	2 951(2)	1 893(3)	−1 830(3)
C(10)	3 553(2)	2 562(3)	−645(3)

Atomic positional parameters of hydrogen atoms ($\times 10^3$)

Atom	*x*	*y*	*z*
H(6)	432	−3	150
H(7)	333	−114	−55
H(8)	242	7	−265
H(9)	261	241	−271
H(10)	360	355	−66

TABLE 2

π-Bond orders and bond lengths in compounds (I)—(IV). The numbering scheme is that of Figure I. The prime refers to the chemically equivalent atom

Bond	Compound	Bond length	Bond order
Endocyclic	(IV)	1.453 (20)	0.39
C(3)–C(4) C(3)–C(4′)	(I)	1.400 (5)	0.45
Endocyclic	(II)	1.373 (10)	0.67
C(2)–C(3)	(I)	1.367 (6)	0.76
C(4)–C(4′)	(I)	1.351 (3)	0.82
Exocyclic	(IV)	1.343 (20)	0.83
C(4)–C(4′)	(III)	1.305(3)	1.00

In (IV) the bond lengths are all equivalent, but the π bonding contribution is greater in the exocyclic bonds [1.34(2) Å] than in the endocyclic one [1.45(2) Å].

The geometry of the $C(CN)_2$ group is close to those of 7,7,8,8-tetracyanoquinodimethane[11] and tetracyanoethylene.[12] The $C{=}C(CN)_2$ bond length of 1.367(6) Å, however, is close to that of 1.374(3) Å in the former, but longer than that of 1.344(3) Å in the latter.

The Bonding Scheme.—A Walsh-type model[13] for cyclopropene is shown in Figure 2(a). Two of the carbon atoms are *sp*-hybridized and one of the remaining two *p* orbitals on each atom is used in forming the double bond. The other *p* orbital contributes to the ring bonding. The third carbon atom remains sp^2-hybridized, one of the hybrids overlapping with one *sp* hybrid of each of the other carbon atoms within the ring. This model was used to interpret qualitatively the differences found in bond lengths of perchloropropene.[15] Such a model, suitably modified, may be adopted to describe in a simple way the electronic structure of (I). As shown in Figure 2(b), all three carbon atoms are assumed to be *sp*-hybridized, each leaving one *p* orbital normal to the ring plane [Figure 2(c)], while the other contributes to the ring bonding as in cyclopropene. Assuming this σ-scheme also applies to (II) and (IV) we can interpret the differences in bond lengths in compounds (I)—(IV) on the basis of different π-bonding contributions.

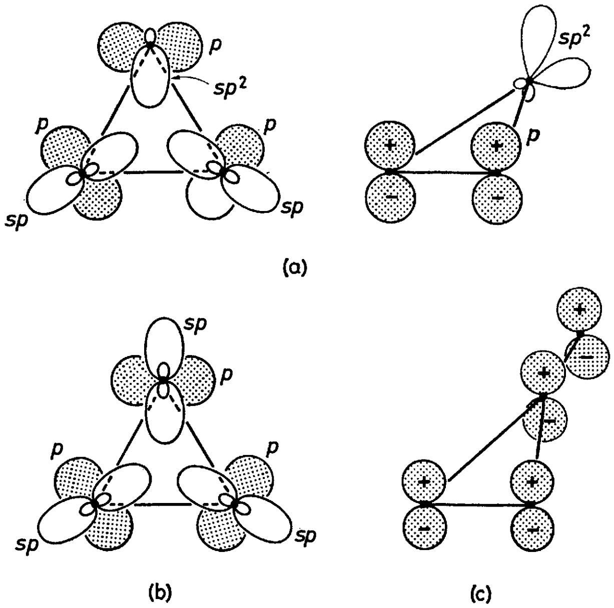


FIGURE 2 Walsh models for cyclopropene (a) and the σ-scheme (b) for molecules having a delocalized π-electron (c)

In fact the three *p* orbitals give delocalized π-orbitals over the D_{3h} ring of (II). The π-bonding scheme for a two-electron, three centre system is shown in Figure 3(a). When the base distance is ‘ compressed ’ and one exocyclic *p*-orbital is added as in (I), the π-bonding scheme for four electrons, with the C_{2v} point group, is modified as illustrated in Figure 3(b). Finally the π-bonding scheme for the six electrons and the six *p* orbitals of (IV) is given in Figure 3(c).

Bond orders, due to the π contribution, are calculated from the coefficients of the respective π-orbitals, shown in Figure 3, for the three compounds, assuming all β values are equal. The trend of π-bond orders follows that of the bond lengths, as shown in Table 2. Furthermore such a scheme suggests a significant degree of π-delocalization over the whole molecule of (I). This is in agreement with the earlier suggestion[2] of a significant contribution by the pseudoaromatic structure (B) to the ground state of the molecule in order to give a high value for the dipole moment. As mentioned in the previous section, the C=C$(CN)_2$ bond length is longer by 0.023 Å than the corresponding distance in tetracyanoethylene. This difference, if significant, further supports such a hypothesis.

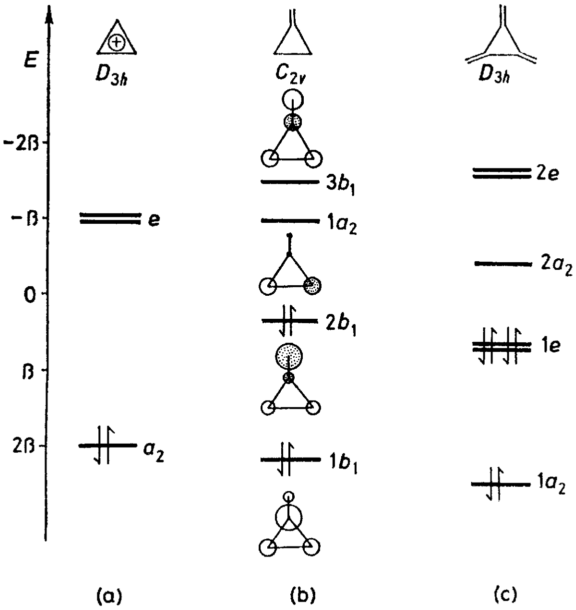
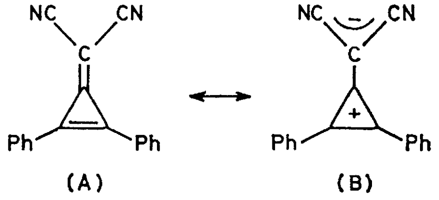


FIGURE 3 π-Bonding schemes for (a) (II), (b) (I), and (c) (IV), assuming $\alpha = 0$ and equal β values in all cases. The π-orbitals in case (b) are also sketched



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