

1,2-Dimethyl-4,4-triafulvenedicarbonitrile†

BY HERMAN L. AMMON AND CAROL SHERRER

Department of Chemistry, University of Maryland, College Park, Maryland 20742, USA

AND THEOPHIL EICHER

Lehrstuhl für Organische Chemie II, Universität Dortmund, D-4600 Dortmund 50, Federal Republic of Germany

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Abstract. $C_8H_6N_2$, $M_r = 130.1$, monoclinic, $P2_1/n$; $a = 7.414$ (1), $b = 15.572$ (1), $c = 7.478$ (1) Å, $\beta = 118.19$ (1)°; $D_c = 1.136$ g cm⁻³ for $Z = 4$; Mo $K\alpha$ diffractometer data. Final $R = 0.041$. The endocyclic C=C distance of 1.327 Å is ca 0.02 Å less than the value found in diphenyltriafulvenes, a difference which appears to be characteristic of the change in the three-membered-ring substituents from phenyl to alkyl. There are no significant differences between the other structural parameters of the 1,2-dimethyl- and 1,2-diphenyl-4,4-triafulvenedicarbonitriles.

Introduction. A sample of 1,2-dimethyl-4,4-triafulvenedicarbonitrile (Ia), prepared in the laboratories of T. Eicher, crystallized from ethanol in the form of colorless blocks. A cube-shaped crystal, ca 0.4 mm in all dimensions, mounted parallel to a , was used for all X-ray measurements. The space group was established with oscillation and Weissenberg photographs with Cu radiation. All lattice-parameter and intensity measurements were made with a Picker FACS-I diffractometer with Mo radiation [graphite monochromator, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å] with the crystal aligned to place a^* parallel to the instrument's φ axis. The final unit-cell parameters were obtained by least-squares calculations from the Bragg angles of 12 reflections manually centered at $\pm 2\theta$ (average of $|2\theta_o - 2\theta_c| = 0.003^\circ$).

Intensities were measured with the $\theta-2\theta$ scan method, with a 2θ scan rate of $2.0^\circ \text{ min}^{-1}$, and with 20 s backgrounds. Three standard reflections were counted at 100-reflection intervals. 1575 data were measured to a 2θ maximum of 50° giving 1340 unique reflections (excluding 63 systematically absent data); 880 of these were 3σ above background. The structure was solved by direct methods with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) subprogram PHASE. The phasing required the calculation of four E maps (corresponding to the four \pm combinations of two

Table 1. Fractional coordinates and e.s.d.'s (in parentheses)

	x	y	z
C(1)	0.2904 (3)	0.1284 (1)	0.5417 (3)
C(2)	0.2475 (3)	0.0984 (1)	0.3598 (3)
C(3)	0.2609 (3)	0.0404 (1)	0.5076 (3)
C(4)	0.2514 (3)	-0.0412 (1)	0.5699 (3)
C(5)	0.2090 (5)	0.1118 (2)	0.1517 (4)
C(6)	0.3364 (5)	0.2006 (2)	0.6852 (5)
C(7)	0.2074 (3)	-0.1118 (1)	0.4364 (4)
C(8)	0.2774 (3)	-0.0578 (1)	0.7668 (4)
N(1)	0.1729 (4)	-0.1698 (1)	0.3308 (3)
N(2)	0.2953 (3)	-0.0729 (1)	0.9244 (4)
H(5A)	0.249 (5)	0.168 (3)	0.130 (5)
H(5B)	0.071 (5)	0.112 (2)	0.062 (4)
H(5C)	0.271 (4)	0.067 (2)	0.108 (4)
H(6A)	0.324 (5)	0.255 (2)	0.611 (4)
H(6B)	0.234 (6)	0.207 (3)	0.732 (6)
H(6C)	0.470 (6)	0.189 (2)	0.805 (5)

unknown starting phases); the best map, computed with 245 phases (121-, 124+), revealed the ten C and N atoms. Structure refinement was by the full-matrix least-squares method minimizing the function $\sum w(F_o - F_c)^2$, where $w = 1$ for $F_o \leq 10$ and $w = (10/F_o)^2$ for $F_o > 10$ (Hughes, 1941). The calculations used anisotropic temperature factors for C and N, and isotropic terms for H. (The initial H atom coordinates were obtained from a difference electron density map.) The F_c 's were corrected for secondary extinction [equation (22) in Larson (1970)], and only those reflections for which $I_c > 3\sigma(I_o)$ were included in the least-squares calculations (1139 data were in this category in the final least-squares cycle). Atomic scattering factors for C and N were obtained from the analytical expressions of Cromer & Mann (1968); the H scattering factors were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). The final R ($\sum |F_o - F_c| / \sum F_o$) and weighted R ($\{[\sum w(F_o - F_c)^2] / \sum wF_o^2\}^{1/2}$) factors were 0.041 and 0.046, respectively. The

† Taken from the PhD dissertation to be submitted by Carol Sherrer to the Graduate School of the University of Maryland.

fractional atomic coordinates are listed in Table 1.* All calculations were carried out on a Univac 1108 computer at the University's Computer Science Center with the XRAY system of programs (Stewart *et al.*, 1972; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. A considerable amount of effort has been devoted in recent years to synthetic, chemical and structural studies of triafulvenes (I) [see Eicher & Weber (1975) for a timely review]. The compounds are intriguing because of the promise of pseudo-aromatic character typified by dipolar structure (II). Although a number of triafulvenes with electron-withdrawing substituents on C(4) [*e.g.* $X = \text{CN}$, CF_3 , $\text{C}(\text{=O})\text{CH}_3$, C_5H_4] and with alkyl or aryl *R* groups have been prepared, characterized and found to be quite stable materials, the parent hydrocarbon (Ib) has not been isolated at this time. A few alkyl-substituted triafulvenes (*e.g.* Ic) are known, but the compounds have only limited stability (Stang & Mangum, 1975; Billups & Blakeney, 1976). We, at the University of Maryland, have been studying fulvene and small-ring molecular structures with X-ray techniques for several years, and our interest in the title triafulvene (Ia) is the determination of the effect of methyl *vs* phenyl three-membered-ring substitution on the structure, and on the relative dipolar character of (Ia) and (Id).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33637 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

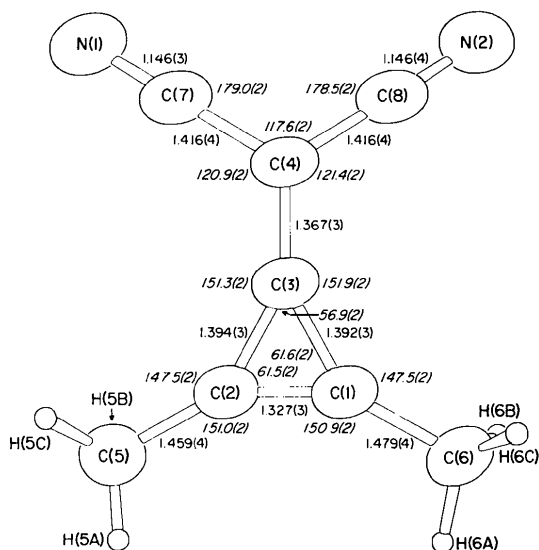
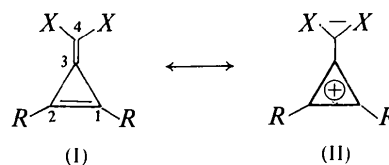


Fig. 1. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses. The C and N atoms are depicted as 30% ellipsoids; H atoms are drawn as 0.1 Å radius spheres.

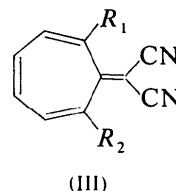
Table 2. Bond lengths (Å) and angles (°) not shown in Fig. 1

C(5)–H(5A)	0.96 (4)	H(5A)–C(5)–H(5B)	102 (3)
C(5)–H(5B)	0.92 (3)	H(5A)–C(5)–H(5C)	112 (3)
C(5)–H(5C)	0.97 (3)	H(5B)–C(5)–H(5C)	107 (3)
C(6)–H(6A)	1.00 (3)	C(1)–C(6)–H(6A)	108 (2)
C(6)–H(6B)	0.98 (5)	C(1)–C(6)–H(6B)	108 (2)
C(6)–H(6C)	0.99 (3)	C(1)–C(6)–H(6C)	112 (2)
C(2)–C(5)–H(5A)	113 (2)	H(6A)–C(6)–H(6B)	117 (3)
C(2)–C(5)–H(5B)	112 (2)	H(6A)–C(6)–H(6C)	108 (4)
C(2)–C(5)–H(5C)	111 (2)	H(6B)–C(6)–H(6C)	103 (3)



- (a) $R = \text{CH}_3$, $X = \text{CN}$ (d) $R = \text{C}_6\text{H}_5$, $X = \text{CN}$
 (b) $R = X = \text{H}$ (e) $R = \text{C}_3\text{H}_7$, $X-X = \text{C}_4\text{Cl}_4$
 (c) $R = X = \text{CH}_3$ (f) $R = \text{C}_6\text{H}_5$, $X-X = \text{C}_4\text{Cl}_4$

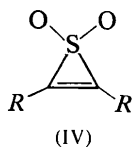
An ORTEP drawing with bond lengths and angles is shown in Fig. 1. Bond lengths and angles not shown on Fig. 1 are given in Table 2. The molecule is planar; the average and maximum deviations of the ten C and N atoms from their least-squares plane are 0.016 and 0.045 Å, respectively. The conformations of the two methyl groups deviate only slightly from the perfectly staggered arrangement suggested in the figure, the rotational deviations being *ca* 15° for C(5) and *ca* 5° for C(6). The C(7)–C(4)–C(8) angle of 117.6° in the title compound and the 119.1° value in the diphenyl analog (Id) (Ammon, 1973) are 3–4° larger than the corresponding angles in 8,8-heptafulvenedicarbonitriles (IIIa–c) (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1966; Shimanouchi, Sasada, Kabuto & Kitahara, 1974a,b). These differences probably reflect a decrease in steric effects in the triafulvenes relative to the heptafulvenes.



- (a) $R_1 = R_2 = \text{H}$
 (b) $R_1 = R_2 = \text{CH}_3$
 (c) $R_1 = \text{H}$, $R_2 = \text{CH}(\text{CH}_3)_2$

The exocyclic C=C [C(3)–C(4)] and endocyclic C–C [C(2)–C(3) and C(1)–C(3)] distances are close to values reported for other triafulvenes and cyclopropenones [a list is given in Table 7 of Eicher & Weber (1975)]. The major bond-length difference is found in the endocyclic C=C [C(1)–C(2)], which at

1.327 Å is *ca* 0.02 Å shorter than this bond in several 1,2-diphenyltriafulvenes. For example, the distance is 1.344 Å in 1,2-diphenyl-4,4-triafulvenedicarbonitrile (Ammon, 1973). Although the difference may reflect some basic changes in the extents of dipolar character in the dimethyl and diphenyl compounds, the change, at least on the surface, appears to be closely related to the nature of the substituent and may involve a hybridization effect, or π -electron delocalization to the aromatic rings. Thus, we note that the endocyclic C=C distance is 1.320 Å in 1,2,3,4-tetrachloro-5,6-dipropylcalicene (Ie) (Shimanouchi, Sasada, Ashida, Kakudo, Murata & Kitahara, 1969) and 1.349 Å in the 5,6-diphenyl analog (If) (Kennard, Kerr, Watson & Fawcett, 1970). Similarly, the C=C distance changes from 1.338 Å in 2,3-dimethylthiirene 1,1-dioxide (IVa) to 1.354 Å in the diphenyl compound (IVb) (Ammon, Fallon & Plastas, 1976). The effect is quite dramatic in the cyclopropenones, in which there is *ca* 0.05 Å increase from cyclopropenone (1.302 Å; Benson, Flygare, Oda & Breslow, 1973) to 2,3-diphenylcyclopropenone (1.349 Å; Tsukada, Shimanouchi & Sasada, 1974). Interestingly, the trend in C=C bond lengths in alkyl- and aryl-substituted alkenes is opposite to that observed in the three-membered-ring compounds. For example, the C=C distances are 1.346 and 1.347 Å in *cis*- and *trans*-2-butene (Almenningen, Anfinsen & Haaland, 1970), *ca* 1.31 Å in *trans*-stilbene (Finder, Newton & Allinger, 1974) and 1.339 Å in 1,2-diphenylcyclopentene (model for *cis*-stilbene) (Bernstein, 1975). The infrared C=C stretching frequencies (Khanna, Ammon & Sherrer, 1978) in (Ia) and (Id) are quite similar at 1872 and 1870 cm^{-1} , respectively.



- (a) $R = \text{CH}_3$
 (b) $R = \text{C}_6\text{H}_5$

The triafulvene C—C and C=C distances in the 1,2-dimethyl- and 1,2-diphenyl-4,4-triafulvenedicarbonitriles are similar and there are no trends to permit an evaluation to be made of the relative degrees of dipolar character in these molecules. The endocyclic C—C lengths are 1.393 and 1.398 Å, respectively, in the methyl and phenyl compounds, whereas the exocyclic C=C's have identical lengths of 1.367 Å. These results, in addition to infrared studies (Khanna *et al.*, 1978) which reveal virtually identical exocyclic C=C stretching frequencies of 1512 and 1510 cm^{-1} for these compounds, suggest that differences in the dipolar

characteristics of the methyl- and phenyl-substituted triafulvenes are not significant.

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