Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Murray-Rust, P., Glen, R. C. & Newton, R. F. (1982). *Acta Cryst.* B**38**, 2702–2704.
Pei, W. W., Pei, J., Chen, J. H., Li, Y. W. & Ye, X. L. (1993). *Acta Sci. Nat. Univ. Peking*, **29**, 129–134.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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1-(8,8-Dicyanoheptafulven-3-yl)aza-15-crown-5 Ether†

KANJI KUBO,[a] NOBUO KATO,[b] AKIRA MORI[b]* AND HITOSHI TAKESHITA[c]*

[a]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221, Japan,* [b]*Institute of Advanced Material Study 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816, Japan, and* [c]*Tohwa Institute for Science, Tohwa University, Minami-ku, Fukuoka 815, Japan. E-mail: mori-a@cm.kyushu-u.ac.jp*

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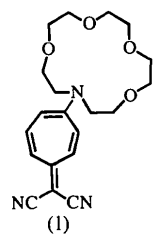
Abstract

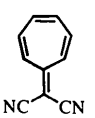
The title compound, $C_{20}H_{25}N_3O_4$, forms a head-to-tail association of two nearly parallel molecules. The bond lengths in the conjugated system indicate a highly polar electronic structure induced by the mesomeric effects of the dialkylamino and dicyano groups.

Comment

Electron-withdrawing groups on the exocyclic double bond of heptafulvene results in a highly polarized structure that induces thermal stability as well as physical and chemical properties such as high dipole moment and deep colouration. We show here the effect of the azacrown ring of the title compound, (1), on the molecular structure of the heptafulvene ring.



(1)



(2)

† Alternative name: 13-[7-(dicyanomethylene)cycloheptа-1,3,5-trien-3-yl]-1,4,7,10-tetraoxa-13-azacyclopentadecane.

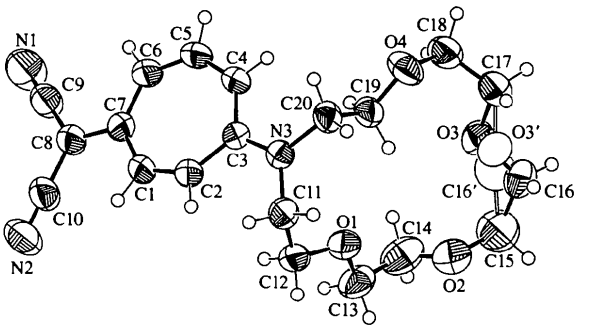


Fig. 1. The molecular structure showing 50% probability displacement ellipsoids. H atoms for the minor component of the disordered contributions have been omitted for clarity.

The structure of (1) and the numbering of the atoms are shown in Fig. 1. The heptafulvene ring of (1) is nearly planar. An ethereal O atom, O3, and its neighboring C atom, C16, are disordered with their counterparts, O3′ and C16′, in the ratio of 68:32. The highly polarized nature of (1) is reflected in the C3—N3 bond length between the azacrown ether and the heptafulvene; the observed value, 1.351 (2) Å, lies between the typical values of CN double (1.269 Å) and single bonds (1.512 Å). The bond alternation of the seven-membered system of (1) is disturbed by the electromeric effect of the azacrown N atom; the bond lengths of C1—C7 and C6—C7 are 1.436 (3) and 1.406 (3) Å, respectively, and the difference, Δd_α = 0.030 Å, is more than experimental error. Even larger differences in the bond lengths are observed for C1—C2 [1.341 (3) Å] and C5—C6 [1.372 (3) Å], Δd_β = 0.031 Å, and for C2—C3 [1.435 (3) Å] and C4—C5 [1.378 (3) Å], Δd_γ = 0.057 Å. Furthermore, the C4—C5 bond [1.378 (3) Å], which is formally a single bond, is shorter than the neighboring C3—C4 [1.401 (3) Å] bond. These differences are explained in terms of the

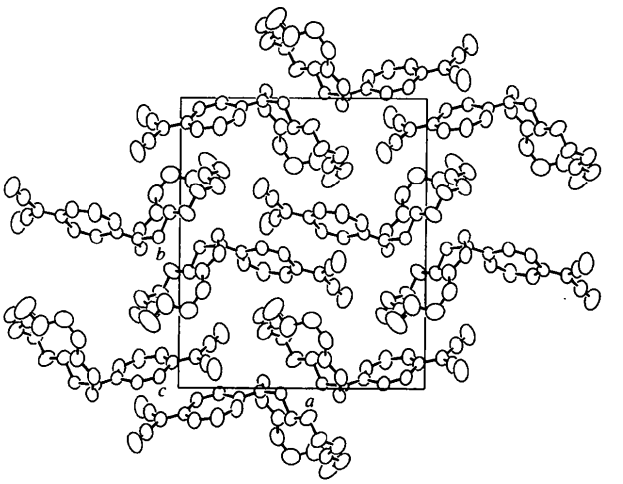


Fig. 2. Packing diagram viewed down the *c* axis. H atoms and the minor component of the disordered contributions have been omitted for clarity.

polarized electronic structure of (1) with enhanced isolated double-bond character for the C1—C2 bond. Interestingly, the bond lengths of the cyano groups and the C7=C8 exocyclic double bond of (1) were almost the same as those of 8,8-dicyanoheptafulvene (Shimanouchi *et al.*, 1966), (2), within experimental error. The mesomeric effect of the N atom in the crown ether apparently does not affect these bond lengths. The crystal packing is shown in Fig. 2, where (1) forms a head-to-tail alignment.

Experimental

A red prismatic crystal of (1), m.p. 407.0–408.5 K (in a sealed tube), was prepared by the condensation of the 3-bromo-8,8-dicyanoheptafulvene with 1-aza-15-crown-5 ether (Kubo, Kato, Mori & Takeshita, 1995) followed by recrystallization from acetonitrile.

Crystal data

$C_{20}H_{25}N_3O_4$
M_r = 371.43
Monoclinic
$P2_1/a$
a = 14.330 (1) Å
b = 16.390 (3) Å
c = 8.484 (1) Å
β = 97.40 (1)°
V = 1976.0 (5) Å^3
Z = 4
D_x = 1.249 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 21–43°
μ = 0.718 mm^{-1}
T = 296 (2) K
Prism
0.50 × 0.30 × 0.25 mm
Red

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.792, T_{max} = 0.836
3598 measured reflections
3355 independent reflections

2672 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 64.96°
$h = -16 \rightarrow 16$
$k = -19 \rightarrow 0$
$l = -9 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.149
S = 1.051
3355 reflections
264 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.5225P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.284 e Å^{-3}
$\Delta\rho_{min}$ = −0.252 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0044 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C9	1.149 (3)	C4—C5	1.378 (3)
N2—C10	1.143 (3)	C5—C6	1.372 (3)
N3—C3	1.351 (2)	C6—C7	1.406 (3)
C1—C2	1.341 (3)	C7—C8	1.408 (3)
C1—C7	1.436 (3)	C8—C10	1.412 (3)
C2—C3	1.435 (3)	C8—C9	1.413 (3)
C3—C4	1.401 (3)		
C3—N3—C20	121.2 (2)	C5—C6—C7	127.9 (2)
C3—N3—C11	122.63 (15)	C6—C7—C8	120.7 (2)
C20—N3—C11	116.19 (15)	C6—C7—C1	121.4 (2)
C2—C1—C7	133.0 (2)	C8—C7—C1	117.9 (2)
C1—C2—C3	132.1 (2)	C7—C8—C10	121.2 (2)
N3—C3—C4	120.3 (2)	C7—C8—C9	122.5 (2)
N3—C3—C2	118.2 (2)	C10—C8—C9	116.3 (2)
C4—C3—C2	121.5 (2)	N1—C9—C8	179.3 (3)
C5—C4—C3	128.4 (2)	N2—C10—C8	178.6 (2)
C6—C5—C4	134.5 (2)		
C7—C1—C2—C3	0.7 (4)	C4—C5—C6—C7	2.6 (5)
C1—C2—C3—C4	9.3 (4)	C5—C6—C7—C1	7.0 (4)
C2—C3—C4—C5	−5.8 (4)	C2—C1—C7—C6	−10.6 (4)
C3—C4—C5—C6	−3.3 (5)		

All H atoms were placed at ideal positions and were included in the refinement, but constrained to ride on the atom to which they are bonded. Isotropic displacement parameters of H atoms were held fixed at 1.2 times U_{eq} of the riding atoms. The disorder ratio of O3 and C16 with their counterparts O3′ and C16′ was also refined in *SHELXL*93 (Sheldrick, 1993). The populations of O3 and C16 were assumed to be the same and this value 0.676 (7) was treated as a 'free variable', while the populations of O3′ and C16′ were fixed at 0.324 (7). The ratio of these sites was then fixed at 0.68:0.32.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1019). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.
Kubo, K., Kato, N., Mori, A. & Takeshita, H. (1995). *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku (Eng. Sci. Rep. Kyushu Univ.)*, **17**, 347–352.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Shimanouchi, H., Ashida, T., Sasada, Y., Kakudo, M., Murata, I. & Kitahara, Y. (1966). *Bull. Chem. Soc. Jpn*, **39**, 2322–2331.