Exceptionally Short Central Bonds in the Cumulogue and the Vinylogue of 2,2-Dicyano-1,1-bis(dimethylamino)ethylene

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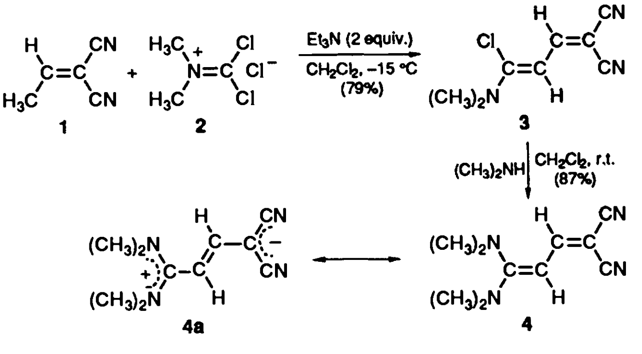
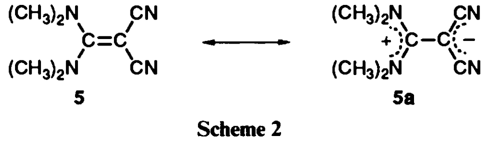
The preparation and crystal structures of twofold push–pull butatriene 2-cyano-5,5-bis(dimethylamino)penta-2,3,4-trienentrile **9** and butadiene 2-cyano-5,5-bis(dimethylamino)penta-2,4-dienenitrile **4** with bis-dimethylamino and dicyano substituents are described. These compounds may be compared with the known corresponding ethylene derivative 1,1-dicyano-2,2-bis(dimethylamino)ethylene **5**. The exceptionally short central bonds in **9** and **4** are in agreement with the earlier proposed concept of cumulogy and of vinylogy to **5**.

Vinylogous activation of the methyl group by cyano substituents is much stronger than by ester substituents.[1] Thus, ethylidenemalononitrile **1** condenses with *N,N*-dimethyldichloromethyleneaminium chloride **2**[2] to the new α-chloro dienamine **3** whereas the diester analogue fails to react.[1] The substitution of the chlorine atom in **3** with *N,N*-dimethylamine leads to the twofold push–pull butadiene **4**[3] (Scheme 1). Compound **4** is the vinylogue[4] of the known 1,1-dicyano-2,2-bis(dimethylamino)ethylene **5** (Scheme 2).[5]

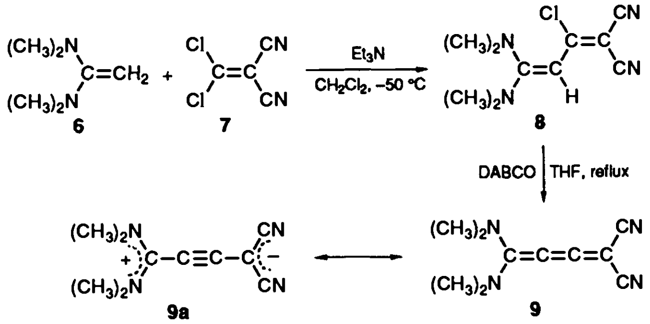

Scheme 1


Scheme 2

The analogous butatriene **9**[3] which is obtained by condensation of 1,1-bis(dimethylamino)ethylene **6**[6] with 1,1-dichloro-2,2-dicyanoethylene **7**[7] is considered as the cumulogue[8] of **5** (Scheme 3).

Compounds **4** and **9** present a highly dipolar character because of an important contribution of the dipolar resonance structures **4a** and **9a**, as expected for efficient twofold push–pull conjugation. The new structures **3**, **4** and **9** were characterized by ^1H and ^{13}C NMR, IR, mass spectrometry and elemental analysis. The purpose of this report is also to document **4** and **9** by X-ray analysis as described in the following discussion.

Figs. 1 and 2 are stereoscopic views of the molecules, showing the numbering of the atoms (program PLUTO[9]). Bond distances and angles are compared in Tables 2 and 3.


Scheme 3

The bond lengths observed in the central part of both molelcules clearly support the concept of vinylogous and cumulogous polar conjunction.

The central bond lengths in the diene **4** indicate a highly dipolar character. Mean values over 76 compounds of Csp^2–Csp^2 single and double bonds in C=C-C=C systems have been calculated by Allen *et al.*:[10] they are, respectively, 1.460(15)Å for C–C and 1.330(14) Å for the C=C double bond. Here we observe a drastically shorter C(3)–C(4) bond of 1.366(2) Å—*i.e.*, 0.1 Å less than expected—and very much longer C(2)=C(3) and C(4)=C(5) bonds of 1.396(2) Å and 1.416(2) Å respectively 0.06 and 0.08 Å more than expected.

Both N atoms have the planar sp^2 configuration as the sums of the valence angles around N(6) and N(11) are 359.8° and 359.7° respectively. The C–N bonds [1.334(2) and 1.353(2) Å] and the C–CN bonds [1.414(2) and 1.409(2) Å] are short and similar to those reported for the push–pull ethylene derivative **5**. As expected in such a conjugated system, the torsion around the single C(3)–C(4) bond joining the two double bonds is 177.2° but the two ethylenic systems are not coplanar as the dihedral angle between the mean planes through C(1),C(2),C(3),C(9) and C(4),C(5),N(6),N(11) has the value of 29°. In conclusion, the diene **4** is best represented by the zwitterionic form **4a**.

X-Ray structures of butatrienes are relatively well documented. In Table 4, the values of the C=C bond lengths for known butatrienes are compared. In all derivatives, the central sp–sp bond is shorter (mean value 1.254 Å) than the sp–sp^2 outer bonds (mean 1.335 Å). For **9**, we observe a central bond of 1.201(2) Å, the shortest ever reported, and outer bonds of 1.377(2) Å and 1.397(2) Å, the longest ever reported. This demonstrates the very high dipolar character of the push–pull butatriene **9** which is best represented by the resonance form **9a**.

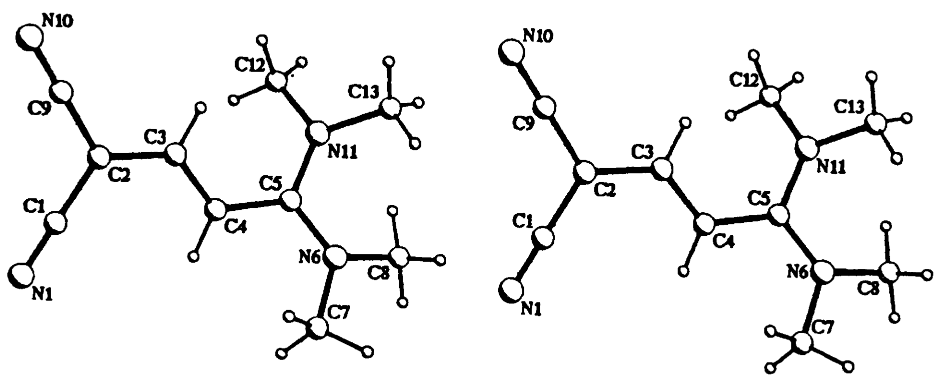


Fig. 1 Stereoscopic view of molecule **4** (PLUTO)[9]

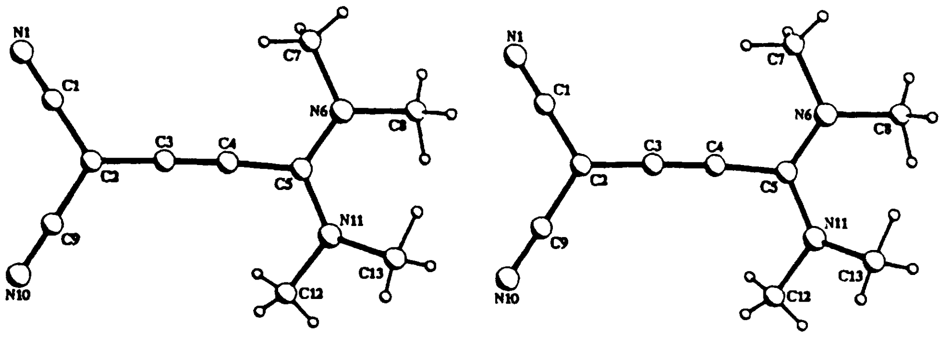


Fig. 2 Stereoscopic view of molecule **9** (PLUTO)[9]

Table 1 Data collection and refinement parameters

	4	**9**
Formula	$C_{10}H_{14}N_4$	$C_{10}H_{12}N_4$
M_r	190.25	188.23
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	7.969(3)	8.356(4)
b/Å	13.590(4)	13.754(5)
c/Å	10.160(4)	9.558(4)
β/deg	100.01(4)	103.44(4)
V/Å^3	1083.5(6)	1068.4(8)
D_x g cm^{-3}	1.17	1.17
Z	4	4
λ	1.54178	1.54178
F(000)	408	400
μ/cm^{-1}	6.03	6.09
Approximate crystal size mm	0.37 × 0.18 × 0.18	0.32 × 0.30 × 0.20
Collection range $(\sin \theta/\lambda)_{max}$/ Å^{-1}	0.60	0.60
Range of hkl	$-9 \leqslant h \leqslant 9$ $0 < k \leqslant 16$ $0 \leqslant l \leqslant 12$	$-9 \leqslant h \leqslant 9$ $0 \leqslant k \leqslant 16$ $0 \leqslant k \leqslant 11$
Indices of standard refl.	2 3 −2	4 0 −4
No. of measured refl.	1909	1925
No. of observed refl. $[I \geqslant 2.5\sigma(I)]$	1690	1633
R	0.054	0.055
w_R	0.066	0.071
$w = 1/(\sigma^2 + gF^2)$; g =	0.02534	0.00004
S	0.62	0.66
(Δ/σ)	0.01	0.01
$\Delta\rho$(max, min) (e Å^{-3})	0.18, −0.30	0.16, −0.27

Table 2 Bond distances (Å)

	4	**9**
C(1)–N(1)	1.139(2)	1.143(2)
C(2)–C(1)	1.414(2)	1.414(2)
C(3)–C(2)	1.396(2)	1.377(2)
C(9)–C(2)	1.409(2)	1.401(2)
C(4)–C(3)	1.366(2)	1.201(2)
C(5)–C(4)	1.416(2)	1.397(2)
N(6)–C(5)	1.334(2)	1.327(2)
N(11)–C(5)	1.353(2)	1.341(2)
C(7)–N(6)	1.450(2)	1.455(2)
C(8)–N(6)	1.451(2)	1.459(2)
N(10)–C(9)	1.144(2)	1.144(3)
C(12)–N(11)	1.459(2)	1.457(2)
C(13)–N(11)	1.445(2)	1.459(2)

The C–N and C–CN bond lengths are similar to those observed in the diene **4**.

As already mentioned for other butatriene derivatives, the chain deviates significantly from linearity, the two C=C=C angles being 178.2(2)° and 174.1(1)°. The butatriene itself is not completely planar: the distances from the mean plane through C(2),C(3),C(4),C(5) are, respectively, C1 = 0.413 Å, C2 = −0.095 Å, C3 = −0.024 Å, C4 = 0.025 Å, C5 = 0.095 Å, N6 = 0.913 Å C9 = −0.620 Å and N11 = −0.665 Å. The dihedral angle between the mean planes through C(1),C(2),C(3),C(9) and C(4),C(5),N(6),N(11) is 17°. With respect to the ethylenic C4=C5 bond, the dimethylamino groups are twisted by 10(1)° and 18(1)°, respectively, for the N6 and N11 substituents.

Figs. 3 and 4 show the packing of the molecules in the unit cell of **4** and **9**, respectively.

Experimental

The ^1H NMR spectra were recorded on a Gemini-200 (200 MHz) spectrometer. The ^{13}C NMR spectra were recorded on a Gemini-200 (50 MHz) spectrometer (J values are given in Hz). The samples were dissolved in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. IR and mass spectra were recorded on a Nicolet-205 and Varian-445SEI apparatus, respectively. Melting points were determined on a Dr. Tottolli apparatus and are uncorrected.

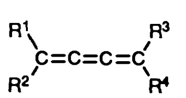
Preparation of 5-*Chloro*-2-*cyano*-5-*dimethylaminopenta*-2,4-*dienenitrile* **3**.—Triethylamine (2.00 g, 20 mmol) diluted in dichloromethane (10 cm^3) was added dropwise over 1 h to a stirred solution of **1** (0.92 g, 10 mmol) and **2** (1.63 g, 10 mmol) in dichloromethane (20 cm^3) at −15 °C. After 15 min at −15 °C, the mixture was warmed to room temperature and washed three times with 20 cm^3 water and once with saturated aqueous NaCl solution. The organic phase was separated, dried (Na_2SO_4) and evaporated to afford a yellow solid. Two recrystallizations of the residue from dichloromethane–ether (1:1) yielded analytically pure material (1.44 g, 79% yield), m.p. 125 °C, δ_H 3.31 (6 H, s), 5.69 (1 H, d, J 11.91) and 7.70 (1 H, d, J 11.96); δ_C 41.5 (qd, J 141.2, J 3.3), 65.9 (d, J 5.8), 94.3 (d, J 159.4), 114.2 (d, J 12.0), 116.2 (d, J 6.7), 153.2 (m) and 156.6 (d, J 159.3); $\nu_{max}(CHCl_3)/cm^{-1}$ 2217, 1558, 1250, 1220 and 1214; m/z (EI): 181 (M^+), 146 ($M^+ - Cl$), 131 ($M^+ - CH_3Cl$), 104, 76 and 43 (Found: C, 52.25; H, 4.35; N, 22.75. $C_8H_8ClN_3$ requires C, 52.90; H, 4.44; N, 23.14%).

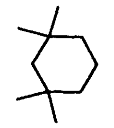
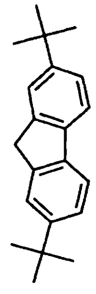
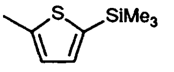
Table 3 Bond angles (deg)

	4	**9**
C(2)–C(1)–N(1)	178.5(2)	179.2(2)
C(3)–C(2)–C(1)	122.1(1)	120.7(1)
C(9)–C(2)–C(1)	117.8(1)	118.0(1)
C(9)–C(2)–C(3)	120.0(1)	121.2(1)
C(4)–C(3)–C(2)	127.0(1)	178.2(2)
C(5)–C(4)–C(3)	121.5(1)	174.1(1)
N(6)–C(5)–C(4)	120.3(1)	120.0(1)
N(11)–C(5)–C(4)	121.6(1)	118.3(1)
N(11)–C(5)–N(6)	118.1(1)	121.8(1)
C(7)–N(6)–C(5)	121.4(1)	120.5(1)
C(8)–N(6)–C(5)	123.4(1)	123.5(1)
C(8)–N(6)–C(7)	115.0(1)	115.2(2)
N(10)–C(9)–C(2)	178.9(2)	179.0(2)
C(12)–N(11)–C(5)	122.2(1)	119.5(1)
C(13)–N(11)–C(5)	122.4(1)	122.6(1)
C(13)–N(11)–C(12)	115.1(2)	113.8(2)

Preparation of 2-*Cyano*-5,5-*bis*(*dimethylamino*)*penta*-2,4-*dienenitrile* **4**.—Dimethylamine (10 cm^3) was dissolved with stirring in a solution of **3** (1.81 g, 10 mmol) in dichloromethane (20 cm^3) at 20 °C. The mixture was stirred for 24 h at room temperature, washed three times with 20 cm^3 water and once with saturated aqueous NaCl solution. The organic phase was separated, dried (Na_2SO_4) and evaporated to give yellow solid which was recrystallized from dichloromethane–ether (1:1) to afford **4** (1.65 g, 87%), m.p. 181 °C, δ_H 3.01 (12 H, s), 4.93 (1 H, d, J 13.55) and 7.15 (1 H, d, J 13.51); δ_C 41.6 (q, J 138.7), 52.3 (d, J 6.4), 89.2 (d, J 158.8), 117.4 (d, J 11.1), 119.8 (d, J 6.0), 155.8 (d, J 152.9) and 168.6 (sm); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2203, 1559, 1529, 1270 and 1019; m/z (EI) 190 (M^+), 175 ($M^+ - CH_3$), 146 ($M^+ - C_2H_6N$), 56 and 42 ($C_2H_4N^+$) (Found: C, 63.05; H, 7.3, N, 29.35. $C_{10}H_{14}N_4$ requires C, 63.13; H, 7.42; N, 29.44%).

Table 4 Bond lengths in butatriene derivatives (Å)



	sp–sp	sp–sp^2	Ref
$R^1 = R^2 = R^3 = R^4 = Ph$	1.259	1.348 —	11
$R_1R_2 = R_3R_4 =$ 	1.261	1.332 —	12
$R^1 = R^2 = R^3 = R^4 = SiMe^3$	1.276	1.319 —	13
$R^1 = R^3 = CF^3$; $R^2 = R^4 = Ph$	1.253	1.333 1.322	14
$R^1R^2 = R^3R^4 =$ 	1.24	1.341 —	15
$R^1 = R^3 = H$; $R^2 = R^4 = Ph$	1.256	1.343 1.322	16
$R_1 = R_2 = R_3 = R_4 =$ 	1.231	1.355 —	17
Mean	1.254	1.335	
$R^1 = R^2 = CN$; $R^3 = R^4 = NMe^2$	1.201	1.377 1.397	This work

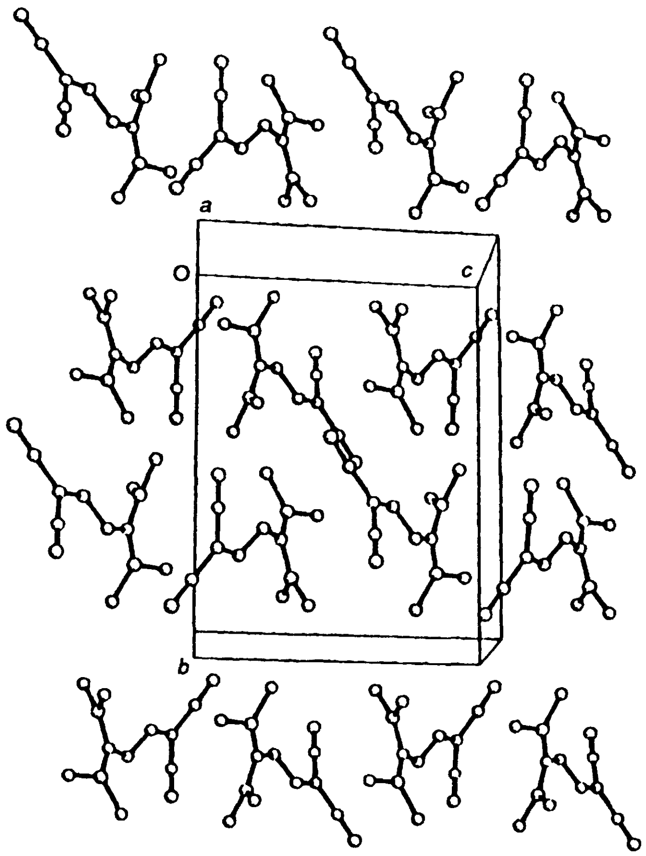


Fig. 3 Packing in the unit cell of **4**[9]

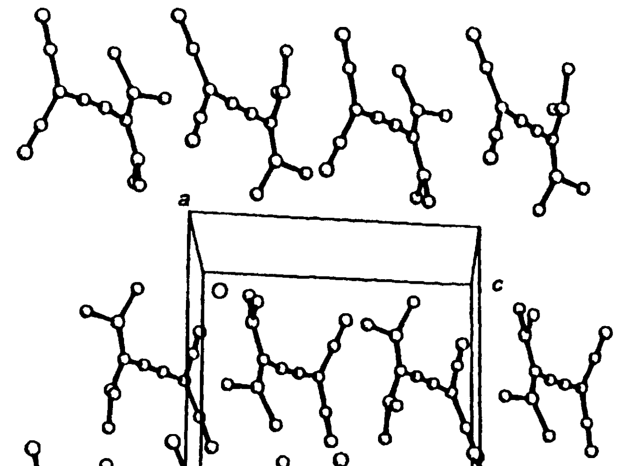


Fig. 4 Packing in the unit cell of **9**[9]

Preparation of 2-*Cyano*-5,5-*bis*(*dimethylamino*)*penta*-2,3,4-trienenitrile **9**.—Compound **7** (1.47 g, 10 mmol) freshly prepared was dissolved in dried dichloromethane and cooled at −50 °C. A mixture of **6** (1.14 g, 10 mmol) and triethylamine (1.11 g, 11 mmol) in dichloromethane (20 cm^3) was added dropwise with stirring. After the addition, the mixture was warmed to room temperature, stirred for 2 h and washed twice with 20 cm^3 water. The organic phase was dried (Na_2SO_4), and evaporated to afford a brown solid (**8**, 1.95 g) which was dissolved in dry THF (20 cm^3). DABCO (1.13 g, 10 mmol) was added and the mixture was refluxed for 24 h. After cooling and filtration, the precipitate (DABCO–HCl) was washed with THF. The combined filtrates were evaporated to give a brown solid which was dissolved in dichloromethane (20 cm^3), washed twice with 10 cm^3 water, dried (Na_2SO_4) and evaporated to afford a yellow solid. Two recrystallizations from dichloromethane–ether (1 : 1) yielded analytically pure material **9** (1.37 g, 76% overall yield), m.p. 166 °C (decomp.), δ_H 3.14 (s); δ_C 22.9 (s), 41.9 (qq, *J* 140.3, *J* 3.4), 93.8 (s), 118.9 (s), 128.9 (s) and 154.2 (br); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2178, 2105 and 1542; *m/z* (EI) 188 (M^+), 173 ($M^+ - CH_3$), 144 ($M^+ - C_2H_6N$), 130, 89, 44 ($C_2H_6N^+$) and 42 ($C_2H_4N^+$) (Found: C, 63.9; H, 6.35; N, 29.9. $C_{10}H_{12}N_4$ requires C, 63.80; H, 6.43; N, 29.76%).

X-Ray Determinations.—Suitable crystals of both compounds were obtained by slow evaporation from dichloromethane–diethyl ether (1 : 1). The crystal data, the data collection and the refinement parameters are summarized in Table 1. The lattice parameters were refined using 22 reflections for **4** and 15 reflections for **9** in the range 25 < 2*θ*/° < 60. A Huber four-circle diffractometer equipped with monochromatized Cu-Kα radiation was used for both data collections. One standard reflection was checked every 50 measurements, no significant deviation was observed. Both structures were solved by direct methods with SHELXS86[18] and refined with SHELX76[19] using *F* values. All hydrogen atoms in both structures were localized by difference Fourier synthesis; they were included in the refinement with common refined temperature factor (U = 0.080 Å^2 for **4** and 0.104 Å^2 for **9**). Atomic scattering factors were taken from *International Tables for X-ray Crystallography*, vol. IV, 1974.

Full lists of atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

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