Unexpected Formation and *X*-Ray Structure of Tetramethyl 4,5-Bis(dimethylamino)-2,3,6,7-tetra-azaocta-1,3,5,7-tetraene-1,1,8,8-tetracarboxylate [$C_{16}H_{24}N_6O_8$] from Bis(dimethylamino)acetylene and Dimethyl Diazomalonate

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Ynediamine (I) reacts with two equivalents of dimethyl diazomalonate thereby forming unexpectedly the ester (III). Its structure was established by *X*-ray analysis: M = 428.40, orthorhombic, $P2_12_12_1$, a = 20.448(6), b = 12.657(5), c = 8.339(4) Å Z = 4, D_x = 1.32 g cm^{-3}, Mo-K_α, λ = 0.710 69 Å, μ = 1.15 cm^{-1}, F(000) = 904, T 291 K, R = 0.067 for 844 observed reflections. Interestingly, both amide azine moieties of (III) are almost perpendicular and no conjugation takes place between them. Diazodibenzoylmethane behaves in the same manner, whereas ethyl diazoacetate (II) forms the expected bis(dimethylamino)pyrazole (IV).

Recently[1] we described a practical single-stage synthesis of bis(dimethylamino)acetylene (I). This electron-rich acetylene is reasonably stable and reacts with a large variety of electrophilic compounds. Owing to this versatility, (I) emerges as a valuable synthon for preparative organic chemistry.[2] Dimethylaminoprop-1-yne fails to react with diazomethane because of unfavourable FMO interactions.[3] On the other hand, both diazoacetate and diazomalonate react smoothly with this ynamine to afford the expected pyrazoles.[4] In the latter case, the resulting 3*H*-pyrazoles undergo the Alpen–Hüttel rearrangement leading to the more stable 1*H*-pyrazoles.[4] We describe herein analogous reactions using (I) as dipolarophile.

Experimental

Preparation of Tetramethyl 4,5-*Bis*(*dimethylamino*)-2,3,6,7-*tetra-azaocta*-1,3,5,7-tetraene-1,1,8,8-*tetracarboxylate* (III).—To a stirred solution of dimethyl diazomalonate[5] (1.32 g, 8.2 mmol) in dry ether (20 ml), a solution of ynediamine (I) (0.46 g, 4.1 mmol) in ether (10 ml) was added dropwise at 0 °C. The mixture was stirred overnight at room temperature. The precipitate was collected, washed with ether, and chromatographed on a silica gel column eluting with chloroform–acetone (1:1 v/v). The solid was recrystallized from ethyl acetate as crystals (0.32 g, 18%), m.p. 179—180 °C (Found: C, 44.65; H, 5.7; N, 19.0. $C_{16}H_{24}N_6O_8$ requires C, 44.85; H, 5.6; N, 19.6%); $\nu_{max.}$($CHCl_3$) 1 740, 1 720, 1 610, and 1 540 cm^{-1}; $\lambda_{max.}$(CH_3OH) 316 nm (ε 40.165); δ_H($CDCl_3$) 2.81 (s), 3.10 (s), 3.70 (s), and 3.78 (s); m/z 428, 397, 369, 337, 309, 284, 181, 139, 69, and 28.

Preparation of 4,5-*Bis*(*dimethylamino*)-3-*ethoxycarbonylpyrazole* (IV).—A solution of ynediamine (I) (1.0 g, 8.9 mmol) and commercial ethyl diazoacetate (II) (1.0 g, 8.9 mmol) in hexane (30 ml) was refluxed for 8 h. The solvent was evaporated off and crude (IV) was distilled in Kugelrohr, b.p. 100 °C at 0.02 Torr. The resulting red viscous oil was chromatographed on a silica gel column eluting with acetone and yielding an orange oil (1.4 g, 70%) (Found: C, 53.2; H, 8.15; N, 24.5. $C_{10}H_{18}N_4O_2$ requires C, 53.1; H, 8.0; N, 24.75%); $\nu_{max.}$(CH_2Cl_2) 3 450 (NH), 1 710, and 1 520 cm^{-1}; $\lambda_{max.}$(hexane) 280 (ε 2 168) and 325 nm (3 060); δ_H($CDCl_3$) 1.33 (t, 3 H), 2.71 (s, 6 H), 2.83 (s, 6 H), 4.26 (q, 2 H), and 10.53 (s, 1 H); m/z 226, 211, 197, 180, and 165.

Preparation of 4,5-*Bis*(*dimethylamino*)-1,8-*diphenyl*-2,3,6,7-*tetra-azaocta*-1,3,5,7-*tetraene*-1,8-*dione* (VI).—A solution of (I) (0.15 g, 1.3 mmol) in ether (10 ml) was added dropwise to an ice-cooled solution of diazodibenzoylmethane[5] (0.67 g, 2.6 mmol) in ether (20 ml). The mixture was stirred overnight at 20 °C, and the precipitate was collected and chromatographed (silica gel, ethyl acetate). The solid was recrystallized from ethanol (0.2 g, 35%), m.p. 189—190 °C (Found: C, 70.6; H, 5.3; N, 13.7. $C_{36}H_{32}N_6O_4$ requires C, 70.7; H, 5.3; N, 14.0%); $\nu_{max.}$(CH_2Cl_2) 2 840—3 070, 1 680, 1 610, and 1 540 cm^{-1}; $\lambda_{max.}$(C_2H_5OH) 254 and 347 nm; δ_H($CDCl_3$) 2.70 (s, 12 H) and 7.00—7.91 (m, 20 H); m/z (d.c.i.; isobutane) 613 (M^+ + 1), 612 (M^+), 376, and 105.

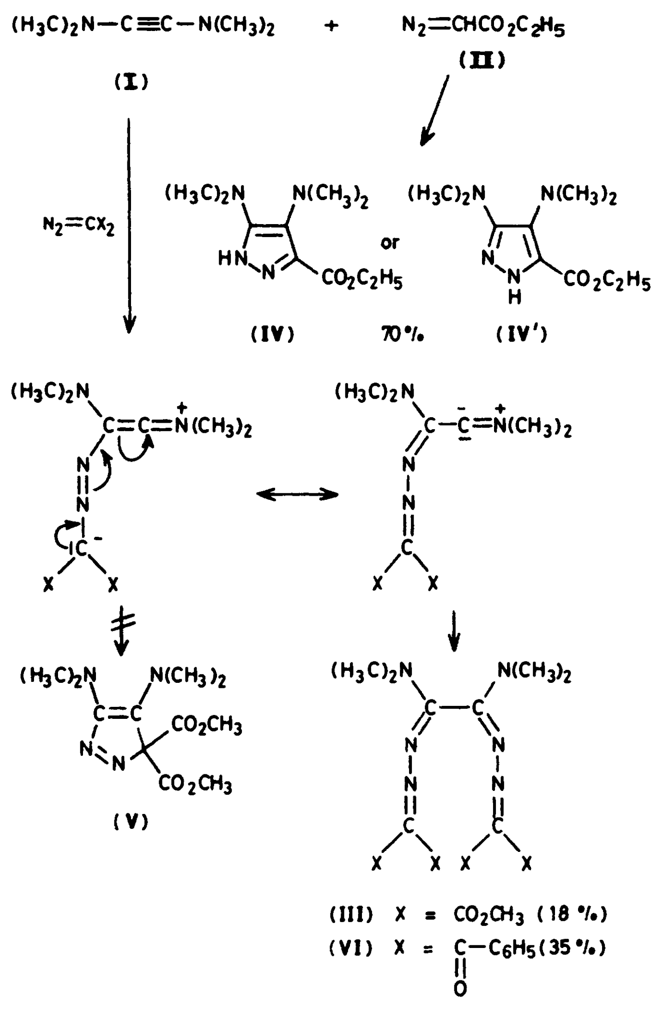
X-*Ray Analysis*.—The unit-cell parameters and their standard deviations were obtained by a least-squares best fit to the setting angles of 15 reflections in the range 5° < 2 θ < 15°. 1 846 Independent reflections with sin θ/λ <0.56 Å^{-1} were collected on a syntex $P2_1$ diffractometer using the ω scan mode and graphite-monochromatized Mo-K_α radiation. Only 844 reflections with $I \geqslant 2.5\sigma(I)$ were conserved for the refinement of the structure. Lorentz and polarization corrections were applied but no absorption corrections were made. The structure was solved by MULTAN 80[6] and refined by full-matrix least-squares analysis first with isotropic and then with anisotropic temperature factors using SHELX 76.[7] Hydrogen-atom positions were computed with C–H distances of 1.08 Å. In the final stage of the refinement a weighting scheme $\omega = 1/(\sigma^2 + 0.002\,69F^2)$ was applied. The final R value was 0.067 and R_ω 0.069 for 844 observed reflections.

Discussion

Ynediamine (I) reacts rapidly with dimethyl diazomalonate in ether to form a rather high melting crystalline product (III) whose n.m.r. displays four singlets of equal intensity. This observation hardly fits with the expected 3*H*-pyrazole structure (V). Unless one dimethylamino group is lost, (I) apparently reacts with two moles of the diazomalonate without nitrogen evolution. The u.v. consists of a conspicuously strong band at 316 nm (ε 40.165). For comparison purposes, we have treated (I) with ethyl diazoacetate (II) to obtain the liquid orange pyrazole (IV) or (IV′) in 70% yield. In this case, only one equivalent of the diazo compound is consumed upon prolonged reflux in hexane. The structure of **(III)** was unambiguously determined by *X*-ray analysis. The push–pull conjugated azine moieties are almost perpendicular to each other. This finding rationalizes the very strong u.v. maximum at 316 nm. The reaction pathway resembles strongly an azo coupling reaction (Scheme).

Diazodibenzoylmethane reacts in complete analogy to diazomalonate to form the mixed azine **(VI)** of oxamide and 1,3-diphenylpropane-1,2,3-trione.

This wholly different reaction path which occurs only with strongly electrophilic diazo compounds is difficult to rationalize. It can be speculated that, owing to the presence of an additional amino group, the intermediate 1,5-dipole is sufficiently nucleophilic to intercept another molecule of diazo



Scheme.

Table 1. Atomic co-ordinates ($\times 10^4$) and equivalent temperature factors (Å^2)

Atom	x	y	z	B_{eq}
C(1)	9 330(7)	4 606(13)	7 838(20)	2.81
N(2)	9 046(5)	3 945(10)	6 896(14)	2.88
N(3)	8 734(5)	3 119(10)	7 724(13)	2.67
C(4)	8 445(7)	2 421(13)	6 897(17)	2.51
C(5)	8 174(8)	1 467(13)	7 718(23)	3.67
O(6)	8 226(6)	1 296(10)	9 131(13)	5.35
O(7)	7 843(5)	895(9)	6 689(11)	4.17
C(8)	7 548(11)	−56(15)	7 339(24)	5.34
C(9)	8 415(7)	2 465(14)	5 092(16)	2.49
O(10)	7 989(5)	2 922(9)	4 373(13)	4.72
O(11)	8 890(5)	1 935(9)	4 409(11)	4.11
C(12)	8 907(8)	1 864(13)	2 657(16)	3.94
N(13)	9 659(7)	5 416(11)	7 302(14)	3.30
C(14)	9 738(9)	5 526(15)	5 542(18)	4.62
C(15)	9 994(8)	6 160(13)	8 313(20)	4.44
C(1′)	9 266(7)	4 520(11)	9 697(17)	2.24
N(2′)	9 722(6)	4 048(10)	10 540(13)	2.93
N(3′)	10 225(6)	3 671(10)	9 541(16)	3.43
C(4′)	10 697(8)	3 254(12)	10 309(17)	2.85
C(5′)	11 245(9)	2 816(13)	9 346(20)	3.87
O(6′)	11 270(6)	2 816(12)	7 893(12)	5.92
O(7′)	11 698(5)	2 392(9)	10 286(13)	4.37
C(8′)	12 239(8)	1 890(15)	9 516(20)	5.10
C(9′)	10 725(9)	3 056(14)	12 142(18)	3.15
O(10′)	10 522(6)	2 294(11)	12 723(13)	5.09
O(11′)	10 992(6)	3 879(9)	12 862(12)	4.36
C(12′)	11 110(11)	3 710(15)	14 609(18)	6.17
N(13′)	8 762(7)	4 950(10)	10 374(13)	2.90
C(14′)	8 682(9)	4 910(14)	12 146(17)	4.30
C(15′)	8 272(7)	5 551(13)	9 465(22)	4.19

$B_{eq} = \frac{8}{3}\pi^2\Sigma_j\Sigma_j U_{ij}a^*_i a^*_j \vec{a}_i\vec{a}_j$

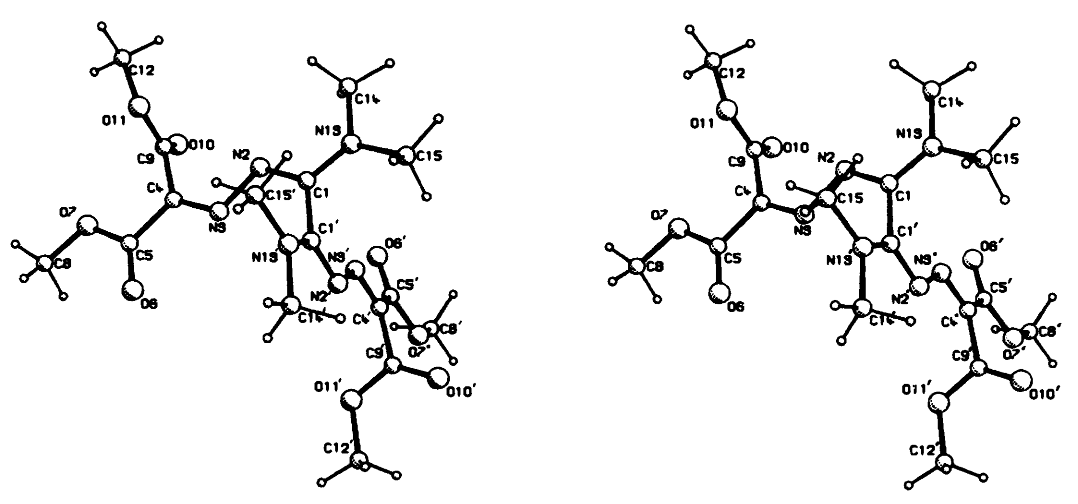


Figure. Stereoscopic view of molecule (III)[9]

Table 2. Bond distances (Å)

N(2)–C(1)	1.29(2)	N(2′)–C(1′)	1.31(2)
N(13)–C(1)	1.31(2)	N(13′)–C(1′)	1.29(2)
C(1′)–C(1)	1.56(2)	N(3′)–N(2′)	1.41(2)
N(3)–N(2)	1.41(1)	C(4′)–N(3′)	1.27(2)
C(4)–N(3)	1.27(2)	C(5′)–C(4′)	1.49(2)
C(5)–C(4)	1.49(2)	C(9′)–C(4′)	1.55(2)
C(9)–C(4)	1.51(2)	O(6′)–C(5′)	1.21(2)
O(6)–C(5)	1.20(2)	O(7′)–C(5′)	1.33(2)
O(7)–C(5)	1.31(2)	C(8′)–O(7′)	1.43(2)
C(8)–O(7)	1.45(2)	O(10′)–C(9′)	1.16(2)
O(10)–C(9)	1.21(2)	O(11′)–C(9′)	1.32(2)
O(11)–C(9)	1.31(2)	C(12′)–O(11′)	1.49(2)
C(12)–O(11)	1.46(2)	C(14′)–N(13′)	1.49(2)
C(14)–N(13)	1.48(2)	C(15′)–N(13′)	1.47(2)
C(15)–N(13)	1.44(2)		

Table 3. Bond angles (°)

N(13)–C(1)–N(2)	122(2)	N(2′)–C(1′)–C(1)	120(1)
C(1′)–C(1)–N(2)	122(2)	N(13′)–C(1′)–C(1)	118(1)
C(1′)–C(1)–N(13)	116(1)	N(13′)–C(1′)–N(2′)	122(1)
N(3)–N(2)–C(1)	113(1)	N(3′)–N(2′)–C(1′)	111(1)
C(4)–N(3)–N(2)	118(1)	C(4′)–N(3′)–N(2′)	113(1)
C(5)–C(4)–N(3)	119(1)	C(5′)–C(4′)–N(3′)	117(1)
C(9)–C(4)–N(3)	122(2)	C(9′)–C(4′)–N(3′)	126(2)
C(9)–C(4)–C(5)	118(2)	C(9′)–C(4′)–C(5′)	117(2)
O(6)–C(5)–C(4)	124(2)	O(6′)–C(5′)–C(4′)	125(2)
O(7)–C(5)–C(4)	110(2)	O(7′)–C(5′)–C(4′)	111(1)
O(7)–C(5)–O(6)	126(2)	O(7′)–C(5′)–O(6′)	124(2)
C(8)–O(7)–C(5)	115(1)	C(8′)–O(7′)–C(5′)	117(1)
O(10)–C(9)–C(4)	123(2)	O(10′)–C(9′)–C(4′)	122(2)
O(11)–C(9)–C(4)	113(1)	O(11′)–C(9′)–C(4′)	110(2)
O(11)–C(9)–O(10)	124(1)	O(11′)–C(9′)–O(10′)	128(2)
C(12)–O(11)–C(9)	119(1)	C(12′)–O(11′)–C(9′)	113(1)
C(14)–N(13)–C(1)	118(2)	C(14′)–N(13′)–C(1′)	121(1)
C(15)–N(13)–C(1)	124(1)	C(15′)–N(13′)–C(1′)	122(1)
C(15)–N(13)–C(14)	118(2)	C(15′)–N(13′)–C(14′)	117(2)

compound rather than to collapse to the putative 3*H*-pyrazole (V).

The atomic parameters of (III) are given in Table 1. The Figure is a stereoscopic view of the molecule, showing the numbering of the atoms.[8] Bond distances and angles are given in Tables 2 and 3 and torsion angles in Table 4. Except the hydrogens, all the atoms of the molecule lie in four planes. The first contains the conjugated chain C(1),N(2),N(3),C(4), the dimethylamino group on C(1),N(13),C(14),C(15), and one ester substituent [C(5),O(6),O(7),C(8)] (maximum deviation from the mean plane 0.15 Å). The same atoms numbered with primes lie in a second plane (maximum deviation from the mean plane 0.10 Å) nearly perpendicular to the first one; the dihedral angle between the two mean planes is 93°. The two other methyl ester substituents [C(9),O(10),O(11),C(12) and C(9′),O(10′),O(11′),C(12′)] are planar and perpendicular respectively to planes 1 and 2 (dihedral angles 88 and 87°). This shows that conjugation takes place in each amidino moiety of the compound and not through the central C(1)–C(1′) bond. The values of the C(1)=N(2), C(1)–N(13), C(1′)=N(2′), and C(1′)–N(13′) bond lengths confirm this scheme of conjugation; within the limit of experimental error, they are identical. The central C(1)–C(1′) bond length of 1.56(2) Å also indicates a non-conjugated single bond.

Table 4. Torsion angles (°)

N(13)–C(1)–N(2)–N(3)	179
C(1′)–C(1)–N(2)–N(3)	−5
N(2)–C(1)–N(13)–C(14)	−4
N(2)–C(1)–N(13)–C(15)	−179
C(1′)–C(1)–N(13)–C(14)	180
C(1′)–C(1)–N(13)–C(15)	5
N(2)–C(1)–C(1′)–N(2′)	97
N(2)–C(1)–C(1′)–N(13′)	−85
N(13)–C(1)–C(1′)–N(2′)	−87
N(13)–C(1)–C(1′)–N(13′)	92
C(1)–N(2)–N(3)–C(4)	180
N(2)–N(3)–C(4)–C(5)	173
N(2)–N(3)–C(4)–C(9)	−1
N(3)–C(4)–C(5)–O(6)	−2
N(3)–C(4)–C(5)–O(7)	174
C(9)–C(4)–C(5)–O(6)	173
C(9)–C(4)–C(5)–O(7)	−11
N(3)–C(4)–C(9)–O(10)	−89
N(3)–C(4)–C(9)–O(11)	93
C(5)–C(4)–C(9)–O(10)	97
C(5)–C(4)–C(9)–O(11)	−81
C(4)–C(5)–O(7)–C(8)	180
O(6)–C(5)–O(7)–C(8)	−3
C(4)–C(9)–O(11)–C(12)	177
O(10)–C(9)–O(11)–C(12)	−1
C(1)–C(1′)–N(2′)–N(3′)	0
N(13′)–C(1′)–N(2′)–N(3′)	−178
C(1)–C(1′)–N(13′)–C(14′)	−179
C(1)–C(1′)–N(13′)–C(15′)	−3
N(2′)–C(1′)–N(13′)–C(14′)	0
N(2′)–C(1′)–N(13′)–C(15′)	175
C(1′)–N(2′)–N(3′)–C(4′)	177
N(2′)–N(3′)–C(4′)–C(5′)	179
N(2′)–N(3′)–C(4′)–C(9′)	6
N(3′)–C(4′)–C(5′)–O(6′)	−1
N(3′)–C(4′)–C(5′)–O(7′)	−179
C(9′)–C(4′)–C(5′)–O(6′)	173
C(9′)–C(4′)–C(5′)–O(7′)	−5
N(3′)–C(4′)–C(9′)–O(10′)	87
N(3′)–C(4′)–C(9′)–O(11′)	−91
C(5′)–C(4′)–C(9′)–O(10′)	−86
C(5′)–C(4′)–C(9′)–O(11′)	95
C(4′)–C(5′)–O(7′)–C(8′)	177
O(6′)–C(5′)–O(7′)–C(8′)	−1
C(4′)–C(9′)–O(11′)–C(12′)	−173
O(10′)–C(9′)–O(11′)–C(12′)	8

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