Aromatic Amines and their Derivatives. Part 3.[1] The Synthesis and Crystal Structure of 4,4'-NN'-Tetramethyl-NN'-dinitroso-2,2'-methylenedianiline
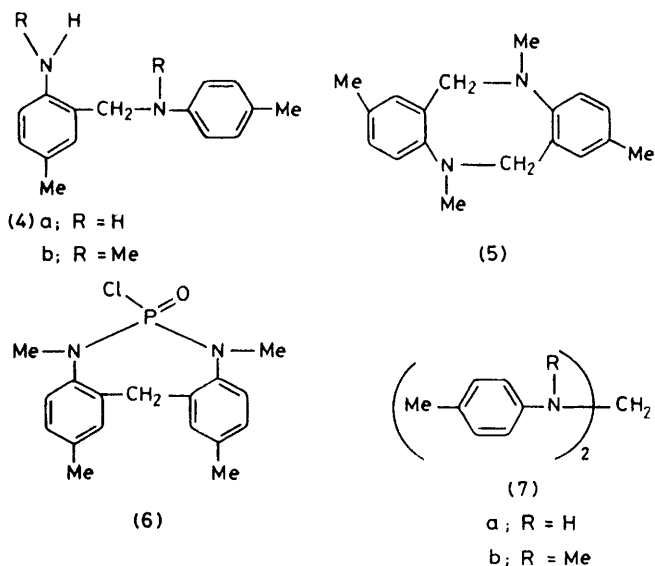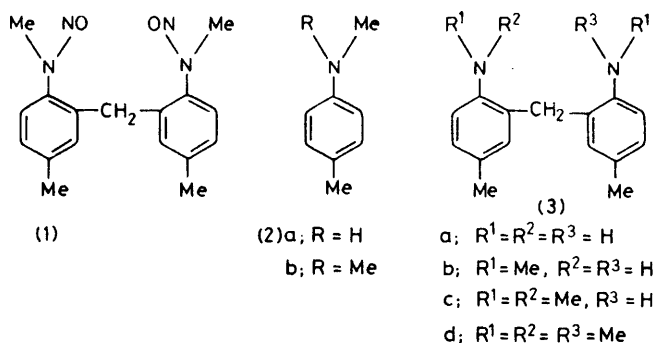
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The synthesis of 4,4',NN'-tetramethyl-NN'-dinitroso-2,2'-methylenedianiline (1) by the route p-MeC$_6$H$_4$NH$_2$ + HCHO + OH$^-$ $\longrightarrow$ (p-MeC$_6$H$_4$NMe)$_2$CH$_2$ (7b); (7b) + acid at 70 °C $\longrightarrow$ 4,N-dimethyl-6-(N-methyl-p-toluidinomethyl)aniline (4b); (4b) + acid at 130 °C $\longrightarrow$ 4,4',NN'-tetramethyl-2,2'-methylenedianiline (3b); (3b) + HNO$_2$ $\longrightarrow$ (1), is described. Aspects of the ^{1}H n.m.r. spectra of the above and related compounds are discussed. A crystal-structure analysis of compound (1) shows one of the N-nitroso-groups to be disordered with the *endo*-form being in preponderance (4 : 1) over the *exo*-form. The other N-nitroso-group is exclusively *exo* in the solid state. There is little or no resonance between the benzene ring and the nitroso-group attached to the ring, the two groups being almost perpendicular to each other. In one of the N-nitroso-groups, the nitrogen atom deviates significantly from the plane of the benzene ring to which it is attached. Both amide nitrogen atoms show some pyramidal character.

THE purpose of this paper is two-fold: (*i*) to clarify the genesis and structure of 4,4',NN'-tetramethyl-NN'-

(1)   (2)a; R = H
       b; R = Me

a; R^1=R^2=R^3 = H
b; R^1=Me, R^2=R^3 = H
c; R^1=R^2=Me, R^3 = H
d; R^1=R^2=R^3 =Me

(4) a; R = H
    b; R = Me

(5)

(6)

(7)
a; R = H
b; R = Me

dinitroso-2,2'-methylenedianiline (1); and (*ii*) to investigate the detailed geometry of the amide nitrogen atoms in this compound.

von Braun [2] was the first to investigate the reaction of N-methyl-p-toluidine (2a) with acidified formaldehyde. He reported the symmetric diamine (3b) as an oily product, which was characterised as its crystalline dinitroso-derivative (1), m.p. 123 °C. More recently Farrar [3] re-investigated the above reaction and reported the diamines (4b) and (5), the former being a precursor of the latter. He failed to observe the symmetric bis(secondary)diamine (3b) reported by von Braun.[2]

The symmetric diamine (3b) has been isolated recently [4] as a crystalline product from the hydrolytic degradation of the eight-membered phosphorus heterocycle (6). As yields of this heterocycle [4,5] obtained from the reaction of phosphorus oxychloride with NN-dimethyl-p-toluidine were poor, we considered that the diamine (3b) was to be a more promising starting material for the synthesis of compound (6).[6]

In view of the contradictions between the findings of von Braun [2] and Farrar [3] we re-investigated the reaction of the secondary amine (2a) with acidified formaldehyde under the conditions specified by Farrar.[3] These types of reactions are notoriously difficult to reproduce;[7] in particular, the nature of the products is dependent on the concentration of the formaldehyde solution and/or acid used. Only the tricyclic heterocycle (5) was observed under most conditions. When the acid concentration was *ca.* 1.5N both compounds, (4b) and (5), were observed. On addition of further formaldehyde to the reaction mixture compound (4b) was rapidly converted into (5). The diamine (3b) was never detected.

RESULTS AND DISCUSSION

Compound (3b) can be conveniently prepared by the method of Wagner [8] and Simons,[9] using a two-stage acid-catalysed rearrangement. The amine (2a) reacts with formaldehyde under alkaline conditions to give the diaminomethane derivative (7b) which rearranges under

acidic conditions at 60—70 °C to the diamine (4b). Further rearrangement, under similar conditions at 130 °C, yields the desired symmetrical diamine (3b). This bis(secondary)diamine (3b) reacts with nitrous acid to give the dinitroso-derivative (1), m.p. 129 °C.

Detailed considerations of the reaction conditions of von Braun [2] and of Farrar [3] now allows a clarification of an apparent contradiction.[10] Farrar's [3] two diamines (4b) and (5), obtained under basic conditions from the reaction mixture are indeed the primary products of the above reaction. von Braun [2] did not neutralise the reaction mixture and consequently an acid-catalysed rearrangement of the diamine (4b) occurred on distillation (b.p. 227 °C at 10 mmHg) to give the symmetrical product (3b).

¹H N.M.R. Spectroscopy.—¹H N.m.r. data for compound (1) and some related diamines are given in Table 1.

TABLE 1

Selected ¹H n.m.r. chemical-shift values (δ from SiMe$_4$) for some diamines (solvent CCl$_4$)

Compound	CH$_2$	NH	NMe	p-Me
(1) [a]	3.89		3.08	2.37
(2a)		3.53	2.52	2.18
(2b)			2.60	2.20
(3a)	3.56	3.40		2.18
(3b)	3.45	3.38	2.72	2.18
(3c) [b]	3.70			
(3d)	4.08		2.61	2.19
(4a)	4.03	3.61		2.21
(4b)	4.10	2.8	2.63	2.21
			2.76	2.25
(5)	4.15		2.76	2.23
(7a)	4.46	3.75		2.20

[a] Solvent CDCl$_3$. [b] Isolated as a by-product in the reaction of phosphorus oxychloride and *NN*-dimethyl-*p*-toluidine (C. Y. Cheng, Ph.D. Thesis, University of London, 1968).

All the methylene signals are singlets. This observation is in contrast to the AB quartet observed for the methylene group of *N*-acetyl-4,*N*-dimethyl-6-(*N*-acetyl-*p*-toluidinomethyl)aniline, a feature that has been attributed [1] to hindered rotation around the phenyl-carbon–amide-nitrogen bond [an AB quartet is also observed in the spectrum of the heterocycle (6)]. The methylene protons are progressively shielded in the structural moieties N–CH$_2$–N < N–CH$_2$–C$_{Ar}$ < C$_{Ar}$–CH$_2$–C$_{Ar}$, as can be seen from the δ values of the two series of compounds (7a), (4a), (3a) and (7b), (4b), (3b). Progressive deshielding occurs for compounds (3c) and (3d). There is one *ortho*-substituted dimethylamino-group in the former and two in the latter compound. The *ortho*-effect will probably hinder or even prevent p_π–p_π overlap by twisting the dimethylamino-group out of the plane of the benzene ring. Thus only the $-I$, and not the $+M$, effect is observed (*cf.* ref. 11 and references quoted therein). The methylene protons of the tricyclic compound (5) have similar shifts to those of the structurally related acyclic analogue (4b). The methylene protons of the dinitroso-derivative (1) are more deshielded than those in the primary (3a) and secondary (3b) amine analogues, but less so than in the tertiary diamine (3d). The NH protons show a slight progressive
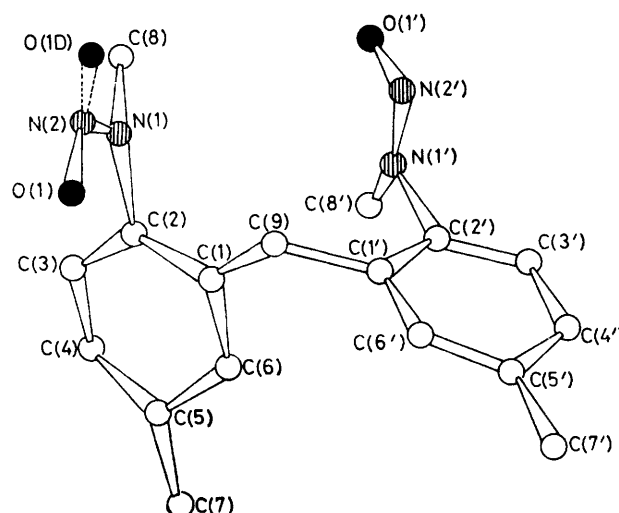

FIGURE 1 Projection of the asymmetric unit viewed along *a*

shielding in the series (7a), (4a), and (3a), paralleling the methylene protons.

X-Ray Crystallography.—Accurate *X*-ray crystallographic investigations of simple peptides have revealed that the atoms of a peptide group need not be as coplanar as had once been thought, and that the nitrogen atom can assume some pyramidal character.[12] It should be worthwhile to investigate the structure of a molecule containing a nominally *sp²*-hybridised nitrogen atom as in the peptide moiety, to see whether this atom

TABLE 2

Bond lengths and bond angles (the second column of values are those for the corresponding primed atoms)

C(1)—C(2)	1.389(3)	1.390(3)
C(2)—C(3)	1.391(4)	1.385(3)
C(3)—C(4)	1.365(4)	1.376(4)
C(4)—C(5)	1.381(4)	1.382(4)
C(5)—C(6)	1.386(4)	1.384(3)
C(6)—C(1)	1.387(3)	1.384(3)
C(5)—C(7)	1.510(5)	1.515(4)
C(2)—N(1)	1.431(3)	1.433(3)
N(1)—C(8)	1.461(4)	1.461(3)
N(1)—N(2)	1.326(4)	1.300(3)
N(2)—O(1)	1.208(4)	1.261(3)
N(2)—O(1D)	1.038(15)	
C(1)—C(9)	1.512(3)	
C(1')—C(9)	1.513(3)	
C(1)—C(2)—C(3)	120.9(2)	120.9(2)
C(2)—C(3)—C(4)	119.6(3)	119.9(2)
C(3)—C(4)—C(5)	121.8(3)	120.5(2)
C(4)—C(5)—C(6)	117.4(3)	118.5(2)
C(5)—C(6)—C(1)	123.0(2)	122.5(2)
C(2)—C(6)—C(9)	121.9(2)	
C(6)—C(1)—C(2)	117.3(2)	117.5(2)
C(6)—C(1)—C(9)	120.7(2)	
C(1)—C(2)—N(1)	120.8(2)	120.7(2)
C(3)—C(2)—N(1)	118.3(2)	118.4(2)
C(4)—C(5)—C(7)	122.4(3)	120.6(2)
C(6)—C(5)—C(7)	120.2(3)	120.8(2)
C(2)—N(1)—C(8)	121.4(2)	120.7(2)
C(2)—N(1)—N(2)	122.2(2)	117.3(2)
C(8)—N(1)—N(2)	116.2(2)	121.6(2)
N(1)—N(2)—O(1)	117.2(3)	113.4(3)
O(1)—N(2)—O(1D)	122.9(8)	
O(1D)—N(2)—N(1)	118.5(8)	
C(2')—C(1')—C(9)	121.5(2)	
C(6')—C(1')—C(9)	121.0(2)	

showed any pyramidal character. The organic nitroso-amines (R_2NNO) afford such a system and we therefore undertook an *X*-ray crystallographic investigation of the title compound, 4,4′,*NN*′-tetramethyl-*NN*′-dinitroso-2,2′-methylenedianiline (1).

Figure 1 shows the perspective view of the molecule. Interatomic distances and interbond angles are given in Table 2.
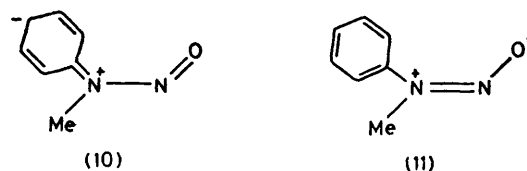
Because of the planarity of the *N*-nitroso-group, the unsymmetrically substituted *N*-nitroso-compounds can exist in an *endo*- (8) or *exo*- (9) conformation, depending on whether the phenyl group is *cis* or *trans* to the nitroso-oxygen. From the occurrence of a single methyl signal
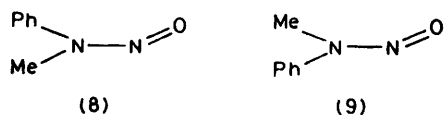
in the [1]H n.m.r. spectrum, Reilly and co-workers [13] suggested a fast rotation about the N–N bond, whereas Karabatos and Taller [14] suggested the exclusive existence of the *exo*-form in solution. In the present molecule, one nitroso-group [N(1′)–N(2′)–O(1′)] occurs in the *exo*-form, whereas the *endo*-form is in preponderance for the other nitroso-group, the *endo* : *exo* ratio being

The two benzene rings in the molecule are almost perpendicular to each other, the angle between them being 89°. The torsional angles, C(2)–C(1)–C(9)–C(1′) = 145.2(2)°, and C(1)–C(9)–C(1′)–C(2′) = −73.8 (2)°. The two phenyl substituents at C(9) have widened the angle C(1)–C(9)–C(1′) to 113.2(2)°.

The angles between the planes containing the nitroso-groups [N(1)–N(2)–O(1), N(1)–N(2)–O(1D), N(1′)–N(2′)–O(1′)] and the planes of the benzene rings to which they are attached are 67, 75, and 85° respectively, showing that there is very little resonance between the benzene rings and their nitroso-groups. This is in contradiction to the suggestion by Reilly [13] that resonance forms such as (10), rather than (11), also contribute to the structure of *N*-nitroso-*N*-methyl-

aniline. The absence of such conjugation was also inferred from u.v. studies [14] on *N*-isopropyl-*N*-phenyl-nitrosoamine. The average N–C(aromatic) bond length
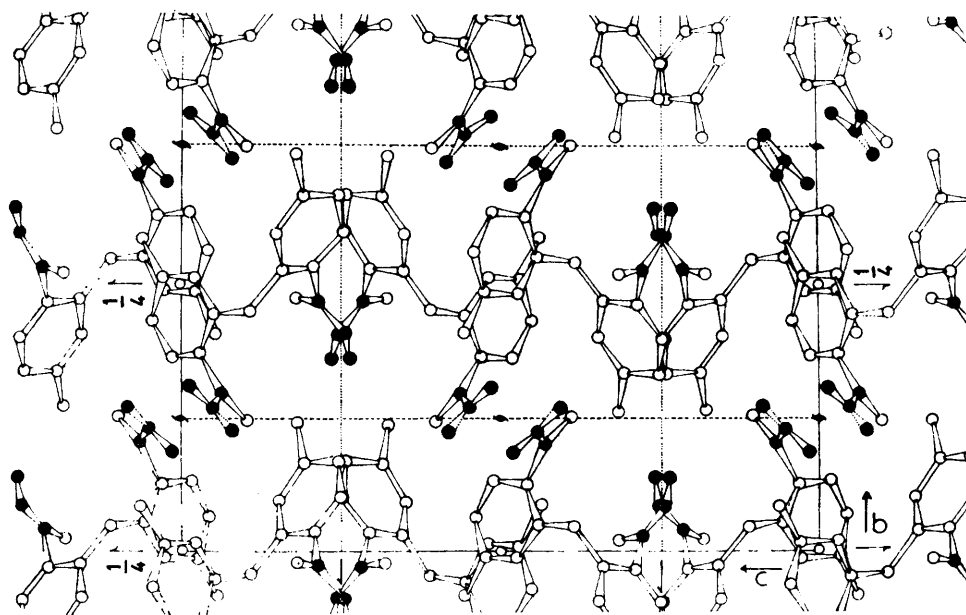

FIGURE 2 The unit cell contents projected down *a*

4 : 1. In the latter case, the *endo*-conformer is favoured because of the presence of an intermolecular interaction [distance 3.05 Å] between C(3) (at *x, y, z*) and O(1D) at ($x - \frac{1}{2}, \frac{1}{2} - y, \bar{z}$).

Figure 2 shows the packing of the molecules in the unit cell. The structure is stabilised by van der Waals interactions. Dimerisation in solution of a type predicted by Reilly and co-workers [13] is not found in the solid state.

of 1.432 (3) Å in this compound corresponds to the value of 1.41 ± 0.02 Å suggested [15] for a σ bond between a trigonal nitrogen atom and a trigonal carbon atom.

The nitrogen N(1′) deviates significantly [0.127 Å] from the best plane of the benzene ring to which it is attached, whereas N(1) deviates only 0.009 Å from the plane of the other benzene ring. The out-of-plane distortions at N(1) and N(1′) from the plane defined by their three bonded neighbours are 0.023 and 0.049 Å,

respectively. The torsion angles at the nitroso-groups are C(2)–N(1)–N(2)–O(1) = 1.2(4), and C(8)–N(1)–N(2)–O(1) = –175.6(3)° for the first nitroso-group [the corresponding angles involving the disordered oxygen atom O(1D) are –166.0(9) and 17.2(12)°, respectively], and C(2')–N(1')–N(2')–O(1') = –175.6(12), and C(8')–N(1')–N(2')–O(1') = –2.6(12)° for the other group. Thus there is evidence for a considerable twist about the N–N bond with N(1) and N(1') both showing some pyramidal character, as observed in the peptide moiety.

The $>$N–N=O group is not completely planar, as can be seen from the deviations of different atoms from the corresponding least-squares planes (Table 3).

TABLE 3

Least-squares planes

(a) Equations of least-squares planes; X, Y, Z are orthogonal co-ordinates (Å) referred to the crystallographic a, b, and c axes

Plane 1: C(2), C(8), N(1), N(2), O(1)
$0.304\,81X - 0.493\,12Y + 0.814\,81Z = 0.4707$

Plane 2: C(2), C(8), N(1), N(2), O(1D)
$0.237\,74X - 0.526\,47Y + 0.816\,28Z = 0.139\,07$

Plane 3: C(2'), C(8'), N(1'), N(2'), O(1')
$0.3570X + 0.498\,76Y - 0.7898Z = -2.071\,12$

(b) Deviations (Å) of atoms from planes

	Plane 1	Plane 2	Plane 3
C(2)	+0.0016	–0.0422	
C(8)	+0.0207	+0.0189	
N(1)	–0.0234	+0.0052	
N(2)	–0.0223	+0.1041	
O(1)	+0.0235		
O(1D)		–0.0859	
C(2')			–0.0242
C(8')			–0.0079
N(1')			+0.0422
N(2')			+0.0081
O(1')			–0.0181

The N–O bond length in nitrosodimethylamine[16] is 1.235(2) Å, whereas in C-nitroso-compounds[17] the average N–O distance is 1.272(6) Å. In the present compound, the N(2')–O(1') distance [1.261(3) Å] is slightly longer than the N(2)–O(1) distance [1.208(5) Å], but correspondingly the N(1')–N(2') distance [1.300(3) Å] is shorter than the N(1)–N(2) distance [1.326(4) Å]. This suggests that a resonance structure such as (11) contributes more to the nitroso-group N(1')–N(2')–O(1') than to N(1)–N(2)–O(1). The average C(methyl)–N bond length of 1.461(4) Å is normal.[16]

The bond angles involving the N-nitroso-groups of the present compound, along with those for nitroso-dimethylamine[16] are as shown. The C–N–N angle involving the carbon atom trans to the nitroso-oxygen is always smaller than the expected value. Depending on the nature of substituents, some of the bond angles in the benzene rings deviate from the normal value of 120°.[18]

In conclusion, a brief comparison of the present structure (1) with the one previously reported[1] (12) will be made. Both diamides are derived from aromatic diamines. Compound (1) can be considered as a derivative of an inorganic acid halide, nitrosyl chloride; compound (12) is derived from an organic acid halide, acetyl

chloride. For acetanilides the phenomenon of cis and trans conformers is well documented.[1] In the diamide (12), both amide groups are in the exo-form as expected for the amide of a secondary aromatic amine. The
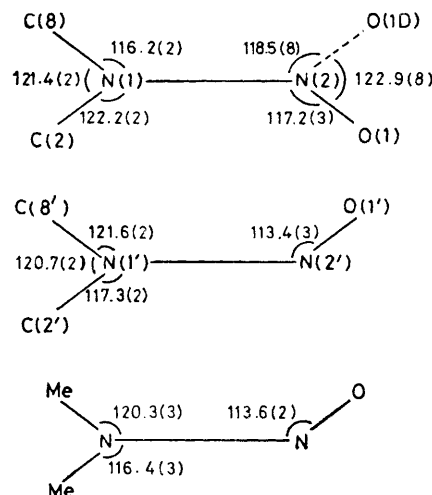
present nitroso-derivative is also based on a secondary amine; its ordered amide group has an exo-conformation, its disordered one a predominantly endo-form (4 : 1). The disorder of the diamide (12) is due to an 180° rotation about the phenyl-carbon–nitrogen-amide bond, the amide oxygen being trans to the phenyl ring in both forms. In contrast, the disorder in the present diamide is due to rotation about the amide-nitrogen–nitroso-nitrogen bond. In the two compounds discussed

(12)
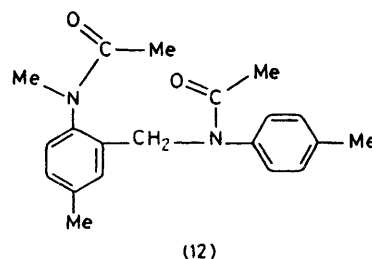
[(1) and (12)], one of the two amide groups is disordered. In both cases, one nitrogen atom deviates significantly from the plane of the benzene ring to which it is attached.

EXPERIMENTAL

Structure Analysis.—The structure was solved by means of the direct multi-solution method, using the program MULTAN.[19] The E map with the highest combined figure-of-merit (CFOM) calculated from 250 reflections with $|E| \geqslant$

1.5 revealed the positions of all the non-hydrogen atoms. The structure was refined by a large-block least-squares method with isotropic temperature factors on all atoms. The refinement converged at $R = 0.13$. All the hydrogen atoms were fixed stereochemically and their positions were located in a difference-Fourier synthesis, which also showed a peak which could be identified as corresponding to the disordered position, O(1D), for one of the oxygen atoms, O(1). The hydrogen atoms were given the isotropic temperature factors of the atoms to which they are bonded and the refinement continued with anisotropic temperature factors on all non-hydrogen atoms. Reflections 200 and 220, which appeared to suffer from extinction effects, were omitted from further calculations. The final R was 0.039 7.

TABLE 4
Atomic parameters ($\times 10^4$, except $\times 10^3$ for hydrogens)

Atom	x	y	z
C(1)	3 485(2)	538(1)	554(1)
C(2)	3 022(2)	1 284(1)	341(1)
C(3)	2 082(3)	1 336(2)	−163(2)
C(4)	1 619(3)	645(2)	−459(2)
C(5)	2 071(3)	−110(2)	−280(1)
C(6)	3 002(2)	−144(1)	227(1)
C(7)	1 574(4)	−879(2)	−606(2)
C(8)	2 671(4)	2 543(2)	1 070(2)
N(1)	3 477(2)	2 018(1)	649(1)
N(2)	4 627(3)	2 280(2)	542(2)
O(1)	5 284(3)	1 879(2)	160(2)
O(1D)	4 968(13)	2 736(9)	866(8)
C(9)	4 463(2)	462(1)	1 125(1)
C(1′)	4 306(2)	−286(1)	1 579(1)
C(2′)	3 366(2)	−342(1)	2 082(1)
C(3′)	3 270(2)	−1 012(1)	2 518(1)
C(4′)	4 076(3)	−1 652(1)	2 434(2)
C(5′)	4 980(3)	−1 634(1)	1 914(1)
C(6′)	5 092(2)	−944(1)	1 504(1)
C(7′)	5 799(3)	−2 364(2)	1 781(2)
C(8′)	1 230(2)	204(2)	1 823(2)
N(1′)	2 455(2)	286(1)	2 150(1)
N(2′)	2 716(3)	885(1)	2 571(2)
O(1′)	1 837(3)	1 384(2)	2 638(2)
H(3)	182(4)	189(3)	−29(2)
H(4)	94(3)	69(2)	−82(2)
H(6)	333(3)	−65(2)	36(2)
H1(7)	134(5)	−76(3)	−11(3)
H2(7)	220(5)	−132(3)	−63(3)
H3(7)	81(6)	−108(4)	−36(3)
H1(8)	239(4)	227(3)	151(2)
H2(8)	321(4)	301(3)	121(2)
H3(8)	196(4)	273(3)	78(2)
H1(9)	443(3)	96(2)	144(2)
H2(9)	526(3)	43(2)	90(2)
H(3′)	262(3)	−102(2)	289(2)
H(4′)	397(3)	−212(2)	272(1)
H(6′)	572(3)	−90(2)	114(1)
H1(7′)	665(7)	−223(4)	165(3)
H2(7′)	566(6)	−280(4)	211(4)
H3(7′)	547(6)	−265(4)	128(3)
H1(8′)	87(6)	−25(4)	214(3)
H2(8′)	66(7)	66(5)	189(4)
H3(8′)	119(6)	−4(4)	135(4)

The weighting scheme was $w = [\sigma^2|F_o| + 0.000\ 3\ |F_o|^2]^{-1}$, where σ is the individual e.s.d. for each reflection and was calculated from the diffractometer counting statistics. The final atomic co-ordinates are given in Table 4; the refined occupancy factor for the two positions O(1) and O(1D) of the disordered oxygen are 0.8 and 0.2 respectively. The anisotropic temperature factors, and observed and calculated structure factors, are available in Supplementary Publication No. SUP 22879 (9 pp.).*

* For details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

Chemicals and Spectroscopic Techniques.—*p*-Toluidine (Koch-Light Ltd.), m.p. 41—44 °C, *N*-methyl-*p*-toluidine (Eastman-Kodak Ltd.), and *NN*-dimethyl-*p*-toluidine (B.D.H. Ltd.) were used without further purification. Formaldehyde was used as a 40% solution (B.D.H. Ltd.) in a mixture of water and methanol (13%). Paraformaldehyde (formalin) and triphenylcarbenium hexafluorophosphate were obtained from Hopkins and Williams, Ltd. and Aldrich Chemical Co. Inc., respectively. For operations requiring anhydrous conditions, ' white spot ' nitrogen was used, which was first passed through a column packed with sodium hydroxide and then through one packed with phosphorus pentaoxide. Solvents were dried by conventional methods. Light petroleum was of b.p. 60—80 °C unless otherwise stated. [1]H N.m.r. spectra were obtained on Varian Associates Model A60 or JEOL Model JNM-MH-100 spectrometers (SiMe$_4$ as internal standard). Mass spectra were obtained on an AEI MS9 mass spectrometer (P.C.M.U., Harwell). Melting points were determined on a Reichert-Kofler microheating stage fitted with a polarising microscope. Microanalyses were carried out by Kolbe Laboratories, Mülheim, Ruhr, Germany.

The syntheses of compounds (4a), (4b), (7a), and (7b) have been described elsewhere.[1]

4,4′-Dimethyl-2,2′-methylenedianiline (3a).—4-Methyl-6-(*p*-toluidinomethyl)aniline (4a) (10 g, 0.044 mol), *p*-toluidine hydrochloride (6.5 g, 0.004 mol), and *p*-toluidine (46.5 g, 0.44 mol), were mixed as solids in a 1 1 three-necked flask fitted with a thermometer and a mechanical stirrer. The mixture was heated under dry nitrogen to 130 °C and maintained at this temperature (9—14 h). On cooling, it was neutralised with NaOH solution. *p*-Toluidine was steam-distilled to leave a tarry residue, which did not solidify upon cooling. The tarry product was dissolved in warm, dilute HCl (1 : 1), the resinous material filtered off, and the filtrate slowly neutralised with NaOH solution to pH 7. The compound then precipitated as an amorphous solid mass. It was filtered off, dried, and recrystallised from light petroleum as colourless needles, m.p. 96 °C (lit.,[8] 96 °C), yield 6.46 g (65%) (Found: C, 79.6; H, 8.0; N, 12.4%; M^+, 226.147 0. C$_{15}$H$_{18}$N$_2$ requires C, 79.6; H, 8.0; N, 12.4%; M^+, 226.147 1).

4,4′-NN′-Tetramethyl-2,2′-methylenedianiline (3b).—4,-*N*-dimethyl-6-(*N*-methyl-*p*-toluidinomethyl)aniline (4b) (0.68 g, 0.002 68 mol), *N*-methyl-*p*-toluidine hydrochloride (0.42 g, 0.002 68 mol), and *N*-methyl-*p*-toluidine (3.24 g, 0.026 8 mol) were mixed in a small flask, heated to 130 °C, and maintained at this temperature for 10 h under nitrogen. The mixture was then neutralised with NaOH solution and the *N*-methyl-*p*-toluidine steam-distilled. The oil obtained failed to crystallise on cooling; it was extracted with warm dilute HCl (1 : 1) and the compound was reprecipitated on basifying this solution with NaOH. Extraction with diethyl ether and removal of solvent gave an oil which solidified on a porous plate and was recrystallised from light petroleum, m.p. 86 °C (lit.,[4] 84—85 °C), yield 0.16 g (23%) (Found: C, 80.3; H, 8.7; N, 11.0%; M^+, 254.177 6. C$_{17}$H$_{22}$N$_2$ requires C, 80.3; H, 8.7; N, 11.0%; M^+, 254.178 3.

4,4′,NNN′N′-Hexamethyl-2,2′-methylenedianiline (3d).—*NN*-dimethyl-*p*-toluidine (2b) (13.5 g, 0.1 mol) was mixed with paraformaldehyde (3 g, 0.1 mol) and 98—100% formic acid (4.6 g, 0.1 mol) in a flask.[20] The mixture was heated on a water-bath until evolution of CO$_2$ ceased (*ca.* 6 h). It was then poured into an aqueous solution of NaOH—

Na_2SO_3. Any remaining (2b) was removed by steam-distillation, and the residue extracted with diethyl ether, dried (Na_2SO_4), the solvent removed, and the oil distilled, b.p. 140—145 °C at *ca.* 1 mmHg (lit.,[20] 205—208 °C at 16 mmHg), yield 9.1 g (64.5%) (Found: C, 80.8; H, 9.2; N, 9.95%; M^+ 282.209 8. $C_{19}H_{26}N_2$ requires C, 80.85; H, 9.2; N, 9.9%; M^+, 282.209 6).

2,5,8,11-*Tetramethyl*-5,6,11,12-*tetrahydrodibenzo*[bf][1,5]-*diazocine* (5).—Triphenylcarbenium hexafluorophosphate (3.88 g, 0.01 mol) was dissolved in dry methylene chloride (25 ml) and added dropwise to a solution of *NN*-dimethyl-*p*-toluidine (excess) in methylene chloride (25 ml) at room temperature under an atmosphere of nitrogen. After 24 h the solvent was evaporated, the oily residue dissolved in diethyl ether, and HCl gas passed through this solution for 2 h. The amine hydrochlorides were filtered off, dissolved in distilled water, the solution basified (NaOH), and *NN*-dimethyl-*p*-toluidine removed by steam-distillation. The remaining oil was crystallised from ethyl alcohol to give colourless needles, m.p. 156 °C (lit.,[3] 149 °C), yield 0.55 g (41%) (Found: C, 81.2; H, 8.3; N, 10.5%; M^+, 266. $C_{18}H_{22}N_2$ requires C, 81.2; H, 8.3; N, 10.5%; M^+, 266).

4,4′,NN′-*Tetramethyl*-NN′-*dinitroso*-2,2′-*methylenedi-aniline* (1).—Concentrated hydrochloric acid (3 ml) was diluted to 50 ml with distilled water, and $NaNO_2$ (0.540 g, 0.007 8 mol) dissolved in this solution. It was then cooled in ice and a solution of 4,4′,*NN*′-tetramethyl-2,2′-methyl-enedianiline (3b) (1 g, 0.003 9 mol) in dilute hydrochloric acid (25 ml) was added with shaking. The mixture was allowed to come to room temperature and neutralised with dilute NaOH, when compound (1) precipitated together with some gummy orange material. It was recrystallised from ethanol by dropwise addition of water. The colourless crystals were dried on a water-bath, m.p. 129 °C (lit.,[2] 123 °C) (Found: C, 65.4; H, 6.35; N, 17.95%. $C_{17}H_{20}N_4O_2$ requires C, 65.4; H, 6.4; N, 17.9%).

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