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# Crystal Structure of Anhydro-2-methyl-4-*o*-nitroanilino-1,2,3-benzotriazinium Hydroxide

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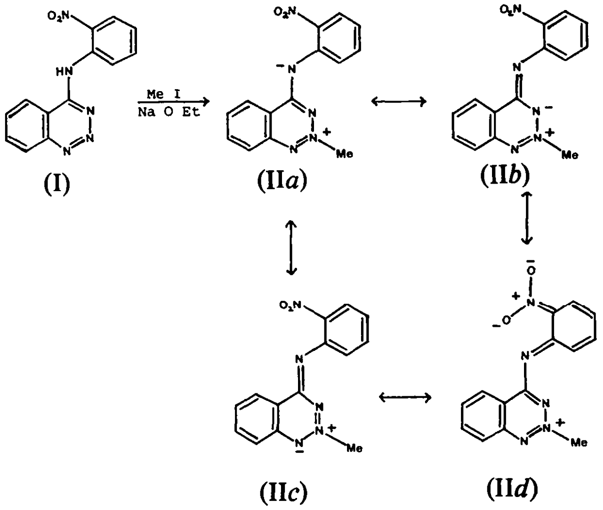
$C_{14}H_{11}N_5O_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 8{\cdot}233\,(3)$, $b = 7{\cdot}764\,(2)$, $c = 20{\cdot}799\,(5)$ Å, $\beta = 93{\cdot}11\,(2)°$, $Z = 4$, $D_c = 1{\cdot}41$, $D_m = 1{\cdot}38$ g cm$^{-3}$. From 1001 observed reflexions measured on a four-circle diffractometer or on Weissenberg films the structure was solved by *MULTAN* and refined by full-matrix least-squares procedures to $R = 0{\cdot}105$, $R_w = 0{\cdot}080$. The benzotriazine ring and exocyclic nitrogen together form a planar delocalized system with the exocyclic C—N distance only 1·29 Å. The bond from this nitrogen to a phenyl carbon is 1·41 Å long and twisted so that the benzotriazine and phenyl planes intersect at 72·5°. The imino character of this nitrogen explains its relatively low basicity.

## Introduction

The stable red title compound (II) was prepared (55%) by reaction of 4-*o*-nitroanilino-1,2,3-benzotriazine (I) with methyl iodide in ethanolic sodium ethoxide solution (Stevens & Stevens, 1970). Compound (II) belongs to a small class of benzotriazinium betaines which can be prepared directly by alkylation (Stevens & Stevens, 1970; Wagner & Gentzsch, 1968) or arylation (McKillop & Kobylecki, 1974) of appropriately substituted 1,2,3-benzotriazines, or indirectly by mild oxidation of *o*-nitrobenzaldehyde arylhydrazones (Kerber, 1972).



Methylation of benzotriazine (I) could involve N(1), N(2), N(3), or the exocyclic N atom, and the evidence supporting structure (II) for the red product was not entirely convincing, being based on spectroscopic and degradative studies (Stevens & Stevens, 1970; Johnstone, Payling, Preston, Stevens & Stevens, 1970). The latter experiments were difficult to interpret because of the possibility for methyl-group rearrangement during degradation. We therefore wanted to verify structure (II) by X-ray diffraction methods, particularly because the related 1,2,3-benzotriazinium iodides (III) exhibit interesting pharmacological properties (Cull & Scott, 1973; French & Scott, 1977). These iodides, on basification, afford intensely coloured, unstable betaines (IV) which are devoid of pharmacological activity. Several contributing structures (II*a*–*d*) can be written for the nitrobenzotriazine with positive formal charge located at N(2) but negative

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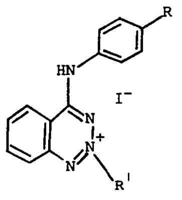
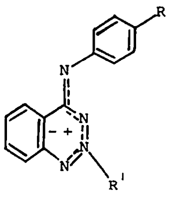
formal charge widely distributed. We have examined the degree of conjugation between the arylimino fragment and the benzotriazine nucleus and sought information on the relative importance of the contributing structures.



(III)

R = H,Me, or Et

R' = Me,Et, or higher alkyl homologues



(IV)

## Experimental

Compound (II) forms small red prismatic crystals elongated along *a*. Unit-cell dimensions were determined by least-squares analysis of four-circle diffractometer measurements at 20 (2)°C.

### *Crystal data*

$C_{14}H_{11}N_5O_2$, $M_r$ = 281·282. Monoclinic, $a$ = 8·233 (3), $b$ = 7·764 (2), $c$ = 20·799 (5) Å, $\beta$ = 93·11 (2)°, $U$ = 1327·54 Å$^3$, $D_m$ = 1·38 (by flotation in aqueous KI), $D_c$ = 1·41 g cm$^{-3}$ with $Z$ = 4, $F(000)$ = 584. Space group $P2_1/c$ (No. 14) from systematic absences of *h*0*l* with *l* odd and 0*k*0 with *k* odd. For Mo *Kα* radiation ($\lambda$ = 0·71069 Å) $\mu$ = 1·08 cm$^{-1}$; for Cu *Kα* radiation ($\lambda$ = 1·5418 Å) $\mu$ = 8·39 cm$^{-1}$.

Structure amplitude data were collected in shells by an $\omega$–$2\theta$ scan on a four-circle diffractometer with Mo *Kα* radiation and a crystal 0·3 × 0·15 × 0·1 mm mounted along *a*. Further data were obtained by microdensitometer evaluation of multiple-film 0*kl* to 4*kl* Weissenberg photographs of a crystal 0·85 × 0·45 × 0·35 mm taken with Cu *Kα* radiation. After Lorentz–polarization correction these data were combined with the diffractometer data having $I > 1{\cdot}5\sigma(I)$ to yield 1001 reflexions in all. No absorption or extinction corrections were found to be necessary.

## Structure determination and refinement

A trial structure was obtained with *MULTAN* (Germain, Main & Woolfson, 1971). All non-hydrogen atoms were subjected to least-squares refinement of coordinates and isotropic temperature factors, with the suspected nitrogen atoms entered as carbon. These and all subsequent calculations were done with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Only five isotropic temperature factors persisted below $U = 2{\cdot}2 \times 10^{-2}$ Å$^2$: those for the five nitrogen atoms in the chemically determined structure (Fig. 1), which thereby receives independent confirmation. Hydrogen atoms were entered in calculated positions guided by a difference electron density synthesis and assigned $U = 6{\cdot}33 \times 10^{-2}$ Å$^2$ for methyl hydrogens and $U = 5{\cdot}70 \times 10^{-2}$ Å$^2$ otherwise. Separate scale factors were applied to data with $2° < 2\theta \le 40°$, $40° < 2\theta \le 47{\cdot}2°$, and $47{\cdot}2° < 2\theta \le 55°$. Atoms were assigned the appropriate scattering factors from *International Tables for X-ray Crystallography* (1968). Final full-matrix refinement of scale factors and non-hydrogen coordinates and anisotropic thermal parameters converged to $R = \sum||F_o| - |F_c||/\sum |F_o| = 0{\cdot}105$ and $R_w = 0{\cdot}080$. Atomic parameter shifts were $0{\cdot}28\sigma$ or less. The function minimized was $\sum w||F_o| - (1/k)|F_c||^2$, and the choice of an appropriate weighting scheme appeared quite important; best results were obtained with $w^{-1} = 1{\cdot}0 + [(F_o - 12)/32]^2$ (Mills & Rollett, 1961) suitably down-weighting the weak data. With this scheme the standard error of an observation of unit weight was 0·977 overall. A difference electron density synthesis

Table 1. *Atomic coordinates in fractions of a unit-cell edge*

(*a*) Non-hydrogen atoms (standard deviations in parentheses)

| | *x* | *y* | *z* |
|---|---|---|---|
| N(1) | 0·2411 (10) | 0·3736 (10) | 0·0056 (4) |
| N(2) | 0·1597 (10) | 0·4021 (10) | −0·0490 (4) |
| N(3) | 0·1267 (9) | 0·5420 (10) | −0·0832 (3) |
| C(4) | 0·1923 (11) | 0·6909 (12) | −0·0584 (4) |
| C(4*a*) | 0·2882 (11) | 0·6830 (13) | 0·0032 (4) |
| C(5) | 0·3582 (11) | 0·8266 (13) | 0·0340 (4) |
| C(6) | 0·4437 (13) | 0·8108 (16) | 0·0916 (5) |
| C(7) | 0·4584 (13) | 0·6460 (20) | 0·1208 (5) |
| C(8) | 0·3934 (14) | 0·5038 (15) | 0·0915 (5) |
| C(8*a*) | 0·3057 (12) | 0·5232 (14) | 0·0325 (4) |
| N(41′) | 0·1757 (9) | 0·8372 (9) | −0·0871 (3) |
| C(1′) | 0·0755 (11) | 0·8536 (9) | −0·1437 (4) |
| C(2′) | 0·1400 (10) | 0·9033 (10) | −0·2016 (4) |
| C(3′) | 0·0421 (12) | 0·9554 (12) | −0·2548 (4) |
| C(4′) | −0·1234 (12) | 0·9490 (12) | −0·2516 (5) |
| C(5′) | −0·1905 (11) | 0·8972 (13) | −0·1954 (5) |
| C(6′) | −0·0920 (11) | 0·8512 (12) | −0·1422 (4) |
| N(2′) | 0·3157 (11) | 0·9033 (13) | −0·2068 (4) |
| O(1) | 0·3950 (8) | 0·7903 (10) | −0·1814 (4) |
| O(2) | 0·3730 (8) | 1·0225 (12) | −0·2368 (4) |
| C(Me) | 0·0896 (13) | 0·2430 (12) | −0·0800 (5) |

(*b*) Hydrogen atoms (not refined)

| | *x* | *y* | *z* |
|---|---|---|---|
| H(5) | 0·348 | 0·943 | 0·013 |
| H(6) | 0·494 | 0·914 | 0·113 |
| H(7) | 0·516 | 0·631 | 0·164 |
| H(8) | 0·408 | 0·386 | 0·111 |
| H(3′) | 0·092 | 0·998 | −0·295 |
| H(4′) | −0·195 | 0·982 | −0·290 |
| H(5′) | −0·312 | 0·892 | −0·193 |
| H(6′) | −0·144 | 0·815 | −0·102 |
| H(21) | −0·013 | 0·253 | −0·059 |
| H(22) | 0·176 | 0·158 | −0·073 |
| H(23) | 0·080 | 0·233 | −0·127 |

showed no feature greater than $\pm 0{\cdot}37$ e Å$^{-3}$. Atomic coordinates are listed in Table 1.*

## Results and discussion

It is obvious from Fig. 1 that the benzotriazine and phenyl rings are far from coplanar. The ten benzotriazine ring atoms deviate only slightly from their least-squares plane ($A < 0{\cdot}03$ Å), as do the six phenyl ring atoms from theirs ($B < 0{\cdot}02$ Å); but the angle between $A$ and $B$ is 72·5° (Table 2). Nitrogen N(41′) is more closely associated with the benzotriazine system [1·29 Å from C(4), 0·03 Å out of plane $A$] than with the phenyl ring [1·41 Å from C(1′), 0·26 Å out of plane $B$]. In terms of $\pi$-electron overlap the nitrophenyl system must be substantially isolated. The geometry about N(41′) is reminiscent of that observed in a careful low-temperature study of *N*-(diphenylmethylene)aniline (TPI) (Tucker, Hoekstra, Ten Cate & Vos, 1975) in which there are a C=N bond 1·287 (4) Å long and a phenyl-N bond of 1·420 (4) Å with a 63·4° twist. The 120·8° bond angle at N(41′) is virtually identical to the 120·6° at N in TPI and suggests $sp^2$ hybridization. The title compound may aptly be called a phenyliminobenzotriazine. A phenylimino substituent on a fused triazole ring has been observed previously (Grout, King & Partridge, 1971).

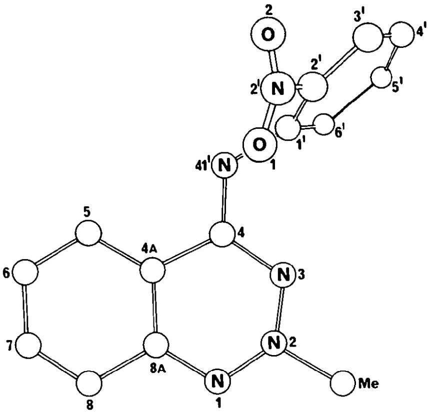


Fig. 1. The molecule and its numbering scheme viewed perpendicular to the benzotriazine plane.

Table 2. *Least-squares planes*

($a$) Equations of planes in the form $AX + BY + CZ + D = 0$ where $X$, $Y$ and $Z$ are orthogonal coordinates in Å along $a$, $b$ and $c^*$

Plane $A$ $-0{\cdot}8636X + 0{\cdot}1497Y + 0{\cdot}4814Z + 1{\cdot}2055 - 0$
Plane $B$ $-0{\cdot}0050X + 0{\cdot}9472Y + 0{\cdot}3207Z - 5{\cdot}3100 = 0$
Plane $C$ $0{\cdot}0488X + 0{\cdot}5400Y + 0{\cdot}8402Z - 0{\cdot}3165 = 0$

($b$) Deviations (Å) of atoms from planes

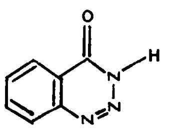
Plane $A$ N(1) −0·014, N(2) 0·000, N(3) 0·021, C(4) 0·000, C(4*a*) −0·014, C(5) −0·008, C(6) −0·002, C(7) 0·023, C(8) −0·002, C(8*a*) −0·004, N(41′)† −0·026, C(1′)† 0·084, C(Me)† −0·028
Plane $B$ C(1′) 0·006, C(2′) −0·017, C(3′) 0·016, C(4′) −0·004, C(5′) −0·007, C(6′) 0·006, N(41′)† 0·259, C(4)† −0·626, N(2′)† −0·059
Plane $C$ N(2′) 0·000, O(1) 0·000, O(2) 0·000, C(2′)† 0·020

($c$) Acute angles (°) between planes

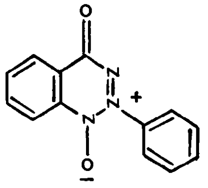
($A$)−($B$) 72·5, ($A$)−($C$) 63·7, ($B$)−($C$) 38·7

† Atom not included in definition of plane.

Bond distances (Table 3) indicate extensive delocalization in the benzotriazine moiety. They may be compared with values for the more localized 1,2,3-benzotriazin-4(3*H*)-one (V) (Hjortås, 1973) and the highly delocalized 4-oxo-2-phenyl-1,2,3-benzotriazinium 1-oxide (VI) (Ballard & Norris, 1975).



(V)



(VI)

In (II) the N(1)—N(2) bond is only 0·01 Å shorter than N(2)—N(3). Corresponding distances are 1·274 (3) and 1·382 (3) Å in (V) but 1·320 (7) and 1·328 (7) Å in (VI). Multiple-bond character in the benzotriazine C—N bonds of (II) is greatest for C(4)—N(41′), less for C(4)—N(3), still less for C(8*a*)—N(1), and essentially non-existent for N(2)—C(Me). In (II), (V) and (VI) alike the strongest C—C bonds are C(5)—C(6) and C(7)—C(8) while by far the weakest (always >1·45 Å) is C(4)—C(4*a*).

Bond angles at the triazine ring nitrogens of (II) (Table 4) follow the predictions of valence state electron pair repulsion theory (Gillespie & Nyholm, 1957) in an extreme form. At the unsubstituted N(1) and N(3) the bond angles are 112·2° and 115·3°, while

Table 3. *Bond distances* (Å) *with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| N(1)—N(2) | 1·31 (1) | C(4)—N(41′) | 1·29 (1) |
| N(2)—N(3) | 1·32 (1) | N(41′)—C(1′) | 1·41 (1) |
| N(2)—C(Me) | 1·50 (1) | C(1′)—C(2′) | 1·40 (1) |
| N(3)—C(4) | 1·37 (1) | C(2′)—C(3′) | 1·39 (1) |
| C(4)—C(4*a*) | 1·47 (1) | C(2′)—N(2′) | 1·46 (1) |
| C(4*a*)—C(5) | 1·39 (1) | C(3′)—C(4′) | 1·37 (1) |
| C(4*a*)—C(8*a*) | 1·39 (1) | C(4′)—C(5′) | 1·38 (1) |
| C(5)—C(6) | 1·36 (1) | C(5′)—C(6′) | 1·38 (1) |
| C(6)—C(7) | 1·42 (2) | C(6′)—C(1′) | 1·38 (1) |
| C(7)—C(8) | 1·36 (2) | N(2′)—O(1) | 1·20 (1) |
| C(8)—C(8*a*) | 1·40 (1) | N(2′)—O(2) | 1·22 (1) |
| C(8*a*)—N(1) | 1·38 (1) | | |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33475 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond angles* (°) *with standard deviations in parentheses*

| | | | |
|---|---|---|---|
| C(8*a*)–N(1)–N(2) | 112·2 (8) | C(8)–C(8*a*)–N(1) | 115·7 (9) |
| N(1)–N(2)–N(3) | 133·7 (8) | C(4*a*)–C(8*a*)–N(1) | 123·0 (8) |
| N(1)–N(2)–C(Me) | 113·8 (7) | C(4)–N(41′)–C(1′) | 120·8 (7) |
| N(3)–N(2)–C(Me) | 112·6 (7) | N(41′)–C(1′)–C(2′) | 120·9 (8) |
| N(2)–N(3)–C(4) | 115·3 (7) | N(41′)–C(1′)–C(6′) | 121·3 (8) |
| N(3)–C(4)–C(4*a*) | 118·5 (8) | C(2′)–C(1′)–C(6′) | 116·9 (8) |
| N(3)–C(4)–N(41′) | 122·8 (8) | C(1′)–C(2′)–C(3′) | 122·3 (8) |
| C(4*a*)–C(4)–N(41′) | 118·7 (8) | C(1′)–C(2′)–N(2′) | 119·4 (7) |
| C(4)–C(4*a*)–C(8*a*) | 117·3 (8) | C(3′)–C(2′)–N(2′) | 118·4 (8) |
| C(4)–C(4*a*)–C(5) | 123·8 (9) | C(2′)–C(3′)–C(4′) | 119·1 (9) |
| C(5)–C(4*a*)–C(8*a*) | 118·9 (8) | C(3′)–C(4′)–C(5′) | 119·7 (9) |
| C(4*a*)–C(5)–C(6) | 120·9 (10) | C(4′)–C(5′)–C(6′) | 120·6 (9) |
| C(5)–C(6)–C(7) | 119·1 (10) | C(5′)–C(6′)–C(1′) | 121·3 (8) |
| C(6)–C(7)–C(8) | 121·2 (9) | C(2′)–N(2′)–O(1) | 119·1 (9) |
| C(7)–C(8)–C(8*a*) | 118·6 (11) | C(2′)–N(2′)–O(2) | 116·7 (8) |
| C(8)–C(8*a*)–C(4*a*) | 121·2 (10) | O(1)–N(2′)–O(2) | 124·2 (9) |

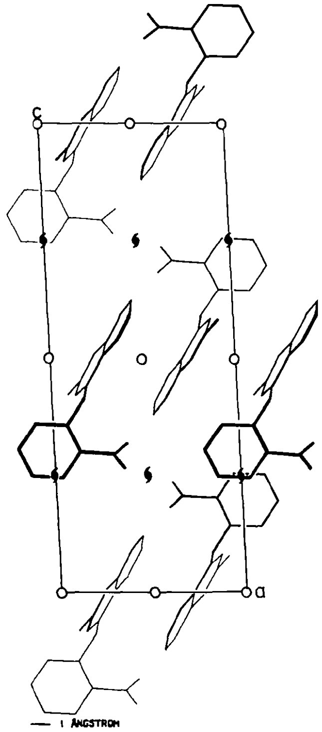

Fig. 2. Packing of molecules in the unit cell viewed along *b*.

at the substituted N(2) the internal angle is 133·7°. Hindrance between N(3) and the nitrophenyl substituent is minimized by opening the exocyclic N(3)–C(4)–N(41′) angle to 122·8°. The nitrophenyl moiety shows, as expected (Domenicano, Vaciago & Coulson, 1975), internal ring angles <120° at the electron-donating substituent (1′) and >120° at the electron-withdrawing one (2′), but with little evidence of conjugative interaction between the substituents. The plane of the nitro group (plane *C*, Table 2) intersects plane *B* at 38·7°, which is not significantly reduced from the average 40° for non-interacting *o*-nitro groups (Holden & Dickinson, 1969). The C–N bond is not unusually short nor is the O···O contact unusually long (Domenicano, Vaciago & Coulson, 1975; Coppens, 1962). One may conclude that contributing structure (II*d*) is irrelevant while (II*b*) and (II*c*) best describe the molecule with (II*a*) not as important.

The packing of molecules in the unit cell is depicted in Fig. 2. By the actions of inversion through a centre of symmetry and translation along *a* the benzotriazine rings are built into stacks with a perpendicular separation between parallel rings of 3·56 Å. The phenyl rings also form columns (along a screw axis), but with a 37·5° angle between normals to successive rings.

We are grateful to Dr P. Main for diffractometer time and help with implementing *MULTAN*, Mr D. Green for sharing apparatus, and the SRC Microdensitometer Service for film evaluation. Computations were carried out at the University of Aston Computer Centre and the University of Manchester Regional Computer Centre.

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