N-Oxides and Related Compounds. Part XL.[1] Chemical and *X*-Ray Crystallographic Investigation of the Oxidation Products of α-Diketone Bisacylhydrazones[2]

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Oxidation of the title compounds yields *O*-acyl imidic acids † derived from 1-amino-1,2,3-triazoles. This structure best explains the chemical and spectroscopic data and is confirmed by an *X*-ray crystallographic study of 1-(α-benzoyloxybenzylideneamino)-4,5-dimethyl-1,2,3-triazole (10). Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 5{\cdot}94 \pm 0{\cdot}03$, $b = 10{\cdot}76 \pm 0{\cdot}05$, $c = 27{\cdot}31 \pm 0{\cdot}14$ Å, $\beta = 100{\cdot}8° \pm 0{\cdot}3°$. The structure was solved by direct methods and refined to R 0·094.

IN 1962, following work on 1,2-dinitroso-compounds,[3,4] we commenced an investigation of 1,2-bisazo-compounds. For *ortho*-substituted benzene derivatives we could show [5] that structures of both types (1) and (2) could be stable, depending on the substituents X and Y: thus the compound with X = Y = Ph exists as (1), but that with X = Ph, Y = CN exists as (2). Dihydrobenzotetrazine structures [*cf.* (3)] previously postulated were found to be incorrect.[5,6]

Three structures (4)—(6) can be drawn for the simpler

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† These compounds were referred to as isoimides in the preliminary communication; [2] we now feel, after consultation with the Editor, that they are better described as imidic acid derivatives.

[1] Part XXXIX, J. Epsztajn, E. Lunt, and A. R. Katritzky, *Tetrahedron*, 1970, **26**, 1665.

[2] Preliminary communication, H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *Angew. Chem.*, 1971, **83**, 115; *Angew. Chem. Internat Edn.*, 1971, **10**, 129.

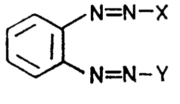
[3] A. R. Katritzky, S. Øksne, and R. K. Harris, *Chem. and Ind.*, 1961, 990.

[4] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J. Chem. Soc.*, 1963, 197.

[5] H. Bauer, G. R. Bedford, and A. R. Katritzky, *J. Chem. Soc.*, 1964, 751.

[6] H. Bauer and A. R. Katritzky, *J. Chem. Soc.*, 1964, 4394.

analogues based on 1,2-bisazoethylenes. Considerable early work (for a summary see ref. 7) had indicated that the bisazo-structure [(4); several geometrical isomers] was applicable to compounds with phenyl groups attached directly to nitrogen, but had assigned dihydrotetrazine structures of type (6) to compounds where $X = Y =$ acyl. In view of our earlier work, the dihydrotetrazine structures (6) appeared improbable, and we therefore reinvestigated the problem of the oxidation product of butane-2,3-dione bisbenzoylhydrazone (7). Oxidation products were readily isolated, from this compound and a variety of substituted derivatives. Structures of type (4) and (6) were excluded by the observation of two methyl peaks in the n.m.r. spectrum. We initially considered this to be evidence for the acyl *N*-imide [*] structure (9), formed by cyclization of the initial bisazo-derivative (8). However, these bisacylhydrazone oxidation products are readily thermally rearranged to 1-(diacylamino)-1,2,3-triazoles: [7] this reaction is most readily explained by invoking rearrangements of the acyl *N*-imide (9) to the imidic acid derivative (10), which itself rearranges to structure (11), although the intermediate (10) is not essential. In the sequence (7) → (8) → (9) → (10) → (11), there is only one isolable intermediate: the n.m.r. evidence excludes this being (8),[†] but it could be either (9) or (10). Curtin and Alexandrou had meanwhile been working independently on the same problem; they interpreted their chemical and spectral evidence in favour of imidic acid-type structures [*cf.* (10)] for the oxidation products initially isolated while realising that their evidence did not rigorously exclude the *N*-imide structure (9).[8-10] The (direct) rearrangement (9) → (11) has analogy in the benzotriazole 1-oxide field; [11] Becker *et al.*[12] have reported the isolation of a 1,2,4-triazole *N*-acylimide (12). Recently, Petersen and Heitzer,[13] have interpreted the evidence in favour of the *N*-imide structure (9) (which they refer to as 'mesoionic') but do not mention the imidic acid possibility (10). The purpose of the present paper is to summarise our own work, extending over the past decade; [14] after considerable chemical effort, we realised that no clear distinction was possible by such means, and we therefore resorted to *X*-ray methods which now finally allow a rigorous structural assignment.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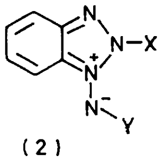
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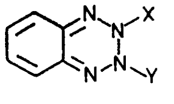
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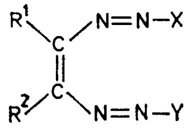
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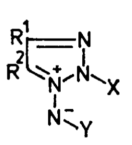
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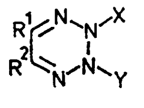
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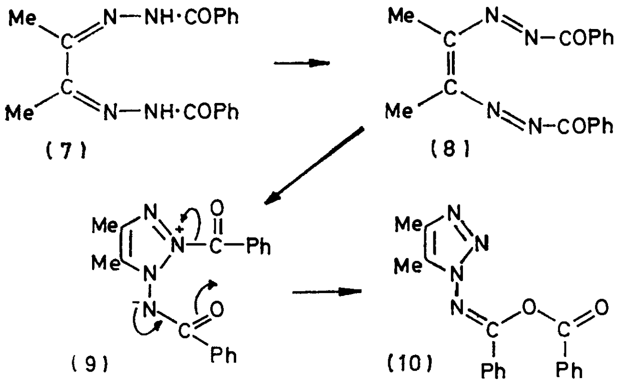
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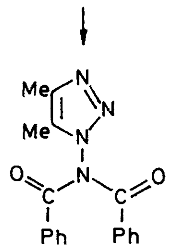
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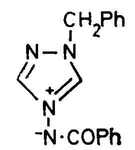
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Chemical Methods for Structural Identification.—(i) We reasoned that the structural ambiguity should not arise for the oxidation products of sulphonylhydrazones of 1,2-diketones, as an imidic acid-type structure is highly unlikely. However, oxidation of the bis-sulphonylhydrazone (14) gave a deep red unstable compound which is clearly the bisazo-derivative (15) and not the *N*-imide (13).

(ii) In an attempted independent synthesis of the imidic acid derivative (10), we treated 1-benzoylamino-4,5-dimethyl-1,2,3-triazole (16) [8,15] with either thionyl chloride or phosphorus pentachloride, but were unable to isolate any crystalline material from the reaction of the presumed intermediate imidic chloride (17) with sodium benzoate.[16]

(iii) We attempted to obtain the asymmetric

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[*] The term '*N*-imide' is used in analogy to '*N*-oxide.' Systematic names for such compounds are of the type '*N*-(2-benzoyl-4,5-dimethyltriazol-1-ylio) benzamidate' (9).

[†] Strictly speaking, *symmetrical* geometrical isomers of (8) are excluded but not the *trans,cis,cis*-isomer on the n.m.r. evidence. However the u.v. spectrum excludes all isomers of (8).

[7] J. G. Erickson, P. F. Wiley, and V. P. Wystrach, 'The Chemistry of Heterocyclic Compounds,' vol. 10: The 1,2,3- and 1,2,4-Triazines, Tetrazines, and Pentazines,' Interscience, New York, 1956, ch. III.

[8] D. Y. Curtin and N. E. Alexandrou, *Tetrahedron*, 1963, **19**, 1697.

[9] N. E. Alexandrou, *Tetrahedron*, 1966, **22**, 1309.

[10] N. E. Alexandrou and E. D. Micromastoras, *Tetrahedron Letters*, 1968, 231.

[11] I. T. Barnish and M. S. Gibson, *Chem. and Ind.*, 1965, 1699.

[12] H. G. O. Becker, N. Sauder, and H. J. Timpe, *J. prakt. Chem.*, 1969, **311**, 897.

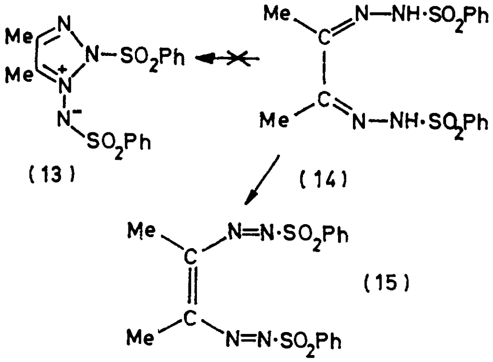
[13] S. Petersen and H. Heitzer, *Angew. Chem.*, 1970, **82**, 81; *Angew. Chem. Internat. Edn.*, 1970, **9**, 67.

[14] See ref. 8, footnote 15 and ref. 9, footnote 5.

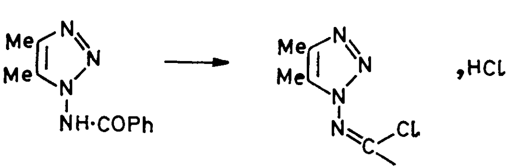
[15] H. V. Pechmann and W. Bauer, *Chem. Ber.*, 1909, **42**, 659.

[16] For full details see A. Majid-Hamid, (*a*) M.Sc. Thesis, 1964; (*b*) Ph.D. Thesis, 1967, University of East Anglia.

hydrazone (19) by condensing dimethylglyoxal monophenylhydrazone (18) with benzohydrazide. However,

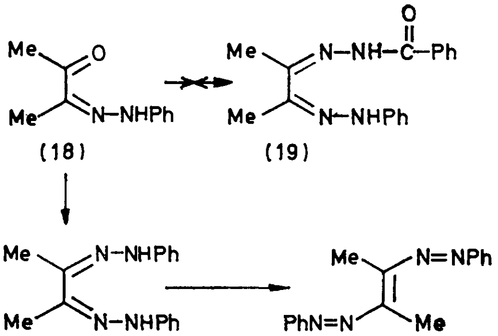


(13) (14) (15)



(16) (17)

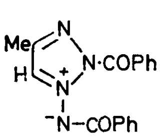
the product was a mixture of the two symmetrical osazones (20) and (7) which could be separated by



(18) (19) (20) (21)

treatment with ethanolic sodium hydroxide in which only (7) is soluble. When the mixture of osazones (20) and (7) was oxidised with potassium ferricyanide, (20) yielded the violet bisazo-compound (21) (m.p. 150—151°). Heating (21) converts it into a yellow isomer (m.p. 230—233°), in what is probably a *cis–trans* conversion. The u.v. spectrum of the violet compound has an absorption maximum ($CHCl_3$) at 379 nm (log ε 4·57), the yellow one at 349 nm (log ε 4·63); the higher wavelength is assigned to the *trans* structure. The i.r. spectra of the two isomers are very similar, as is usual for stereoisomers: the tetrazine structure formerly[17] assigned to the violet compound is thus excluded also for the yellow isomer. The n.m.r. spectrum of the violet compound shows a singlet methyl peak at τ 7·38 ($CHCl_3$); the yellow compound a singlet at τ 7·80 ($CHCl_3$). Compounds containing two *cis* hydrogen atoms or methyl groups at a C=C double bond possess τ values higher than the corresponding *trans* forms.[18]

N.m.r. Evidence.—(i) The oxidation product of the bishydrazone (7) showed methyl peaks in the n.m.r. spectrum at τ 7·65 and 7·78, in agreement with the other workers who quote 7·65 and 7·75 [8] and 7·64 and 7·77.[13] The conversion of this (and other) oxidation products into the corresponding 1-(dibenzoylamino)triazole (11) could be followed in the n.m.r. spectrum. Now, the 4,5-bond order in the imidic acid structure should be similar to that in the (dibenzoylamino)-compounds, but the 4,5-bond order should be lower for the *N*-imide structure. Such a criterion was recently applied in the triazole field by Ykman *et al.*[19] We therefore oxidised methylglyoxal bisbenzoylhydrazone and obtained one product [20] in which the methyl group was assumed to be in the 4-position of the triazole ring and which thus had structure (22) or (23) (the argument is not affected if the methyl group is alternatively in the 5-position). The methyl-hydrogen to ring-hydrogen coupling was found to be 0·8 Hz for both the oxidation product and the thermally rearranged product (24); this suggests that the structure for the oxidation product is (23) and not (22).



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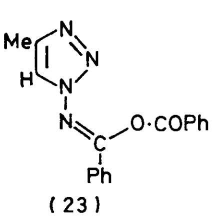

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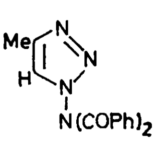

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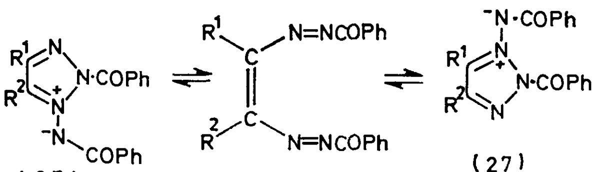

(25) (26) (27)

(ii) If *N*-imide structures [*cf.* (9)] were correct, there is the possibility of a rearrangement [(25) $\rightleftharpoons$ (27)] *via* (26) as a transient intermediate, similar to that found for benzofuroxans [21] and furoxans.[22] Such a rearrangement is not fast on the n.m.r. time scale, as the oxidation product in the dimethyl series shows no coalescence of the methyl peaks at temperatures up to 110°. The bisbenzoylhydrazone of pentane-2,3-dione yielded two isomeric oxidation products: if these were *N*-imides they would possess structures (25) and (27) (R^1 = Me,

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[17] H. von Pechmann, *Ber.*, 1888, **21**, 2751.

[18] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 1960, 2886.

[19] P. Ykman, G. L'Abbe, and G. Smets, *Tetrahedron Letters*, 1970, 5225.

[20] R. Stollé, *Ber.*, 1926, **59***B*, 1742.

[21] For a review, see A. J. Boulton and P. B. Ghosh, *Adv. Heterocyclic Chem.*, 1969, **10**, 1.

[22] F. B. Mallory and A. Cammarata, *J. Amer. Chem. Soc.*, 1966, **88**, 61.

R^2 = Et). No conclusive evidence for the interconversion of these two oxidation products could be detected in the n.m.r. spectra after heating for various periods.[16]

X-Ray Crystallographic Study.—(With technical contribution from Mr. N. Ocello.) Well shaped, colourless, prismatic, monoclinic crystals of the oxidation product which can be isolated during the conversion of butane-2,3-dione bisbenzoylhydrazone (7) into 1-(dibenzoylamino)-4,5-dimethyl-1,2,3-triazole (11) were obtained by slow evaporation at room temperature from water–ethanol.

Crystal data are: $C_{18}H_{16}N_4O_2$, $M = 320{\cdot}35$, Monoclinic $a = 5{\cdot}94 \pm 0{\cdot}03$, $b = 10{\cdot}76 \pm 0{\cdot}05$, $c = 27{\cdot}31 \pm 0{\cdot}14$ Å, $\beta = 100{\cdot}8° \pm 0{\cdot}3°$, $U = 1714{\cdot}8$ Å^3, $D_m = 1{\cdot}23$ (by flotation), $Z = 4$, $D_c = 1{\cdot}24$, $F(000) = 672$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) $= 6{\cdot}93$ cm^{-1}. Oscillation and Weissenberg photographs were taken. The errors quoted for cell dimensions are maximum errors.

The intensity data of 1576 independent non-zero reflections (*ca.* 41% of those possible within the Cu-K_α sphere) were estimated visually from Weissenberg photographs taken with nickel-filtered Cu-K_α radiation, by use of two crystals mounted along the a (layers 0—$4kl$) and b (layers $h0$—$6l$) axes respectively. Current Lorentz, polarisation and spot-extension[23] corrections were applied, and inter-layer scaling,[24] but not absorption nor extinction. Observed structure amplitudes were put on an approximate absolute scale by a Wilson plot.

The overall temperature factor obtained from the Wilson plot was used to generate normalised structure factors $|E_{hkl}|$ from the observed structure amplitudes. A direct method technique developed by one of us[25] and which makes use of Sayre's equation, was applied to some 300 reflections with the highest $|E_{hkl}|$ values. The set of phases thus obtained was used to calculate an E-map from which all the non-hydrogen atoms were located. After a first block-diagonal (4×4) least-squares refinement of the positions of the atoms, to which carbon form-factors and an overall isotropic temperature factor were assigned, the chemical species were assigned from chemical evidence and by electron population analysis of the peaks found in a Fourier synthesis calculated at this stage. Four further cycles of least-squares refinement were then calculated with individual form-factors and invividual thermal isotropic parameters, leading to R 0·14. Six cycles of anisotropic block-diagonal (9×9) least-squares refinement reduced R to 0·105. A difference Fourier synthesis computed at this stage showed residual electron density in all the positions expected for hydrogen atoms. A final refinement in which the hydrogen atoms were assumed to vibrate isotropically with a fixed common B value of 4 Å^2 lowered R to 0·094. During the refinement the weighting scheme $w = [a + |F_o| + b|F_o|^2]^{-1}$ was used, the values of a and b being adjusted by means of a least-squares procedure, in order to keep the mean values of $w|\Delta F|^2$ approximately constant over equally populated regions of F_o. A final difference Fourier synthesis showed no positive nor negative electron density residuals in the neighbourhood of the non-hydrogen atoms. Atomic scattering factors for oxygen, nitrogen, and carbon were taken from ref. 26 and for hydrogen from ref. 27, and the calculations were carried out on the UNIVAC 1108 computer of Rome University, using the programme library[28] of the Laboratorio di Strutturistica Chimica 'Giordano Giacomello.'

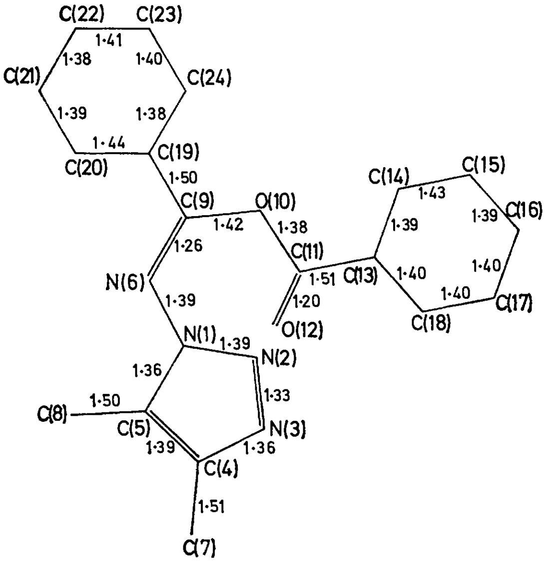

FIGURE 1 Bond lengths, omitting hydrogen atoms, determined for molecule (10)

All the relevant data defining the molecular geometry and packing, and the observed structure amplitudes and calculated structure factors are published in Supplementary Publication SUP 20310 (14 pp., 1 microfiche),* which includes final positional parameters, final anisotropic temperature factors for non-hydrogen atoms, observed structure amplitudes and calculated structure factors, bond lengths and angles, relevant least-squares planes, internal rotation angles within the main chain of the molecule, and intermolecular contacts <3·50 Å.

The intramolecular bond lengths and angles for non-hydrogen atoms are shown in Figures 1 and 2, together with the crystallographic numbering used in the analysis. The estimated standard deviations are in general 0·01 Å

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, issue No. 20.

[23] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[24] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[25] W. Fedeli, Atti del IV Convegno dell'Associazione Italiana di Cristallografia, Cagliari, 1970, p. 13.

[26] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **24**, 321.

[27] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[28] A. Domenicano, R. Spagna, and A. Vaciago, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 331.

and 0·6° for the bond lengths and angles not involving hydrogen atoms. The mean value of the aromatic carbon–carbon bonds for both benzene rings is 1·40 Å and none of the other bond lengths and angles deviate significantly from generally accepted values. Structure (10) is therefore established beyond doubt, and a perspective model of it is shown in Figure 3, where the vibrational ellipsoids are drawn at the 50% probability level.

In each individual molecule the main chain, *i.e.* the sequence N(6)–C(9)–O(10)–C(11), forms a helix-like chain. The triazole ring and the benzene ring attached to C(9) lie in planes whose dihedral angle is 18·5°, whilst the angle between the triazole ring and the benzene ring attached to C(11) is 65·5°. The dihedral angle between the mean planes of the two benzene rings is 58·4°.

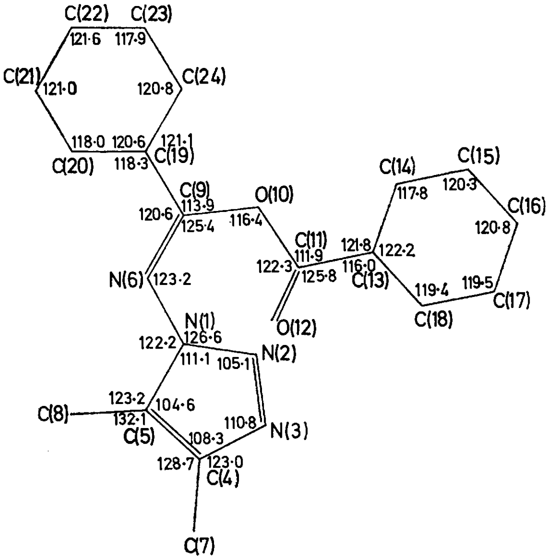

FIGURE 2 Bond angles, omitting hydrogen atoms, determined for molecule (10)

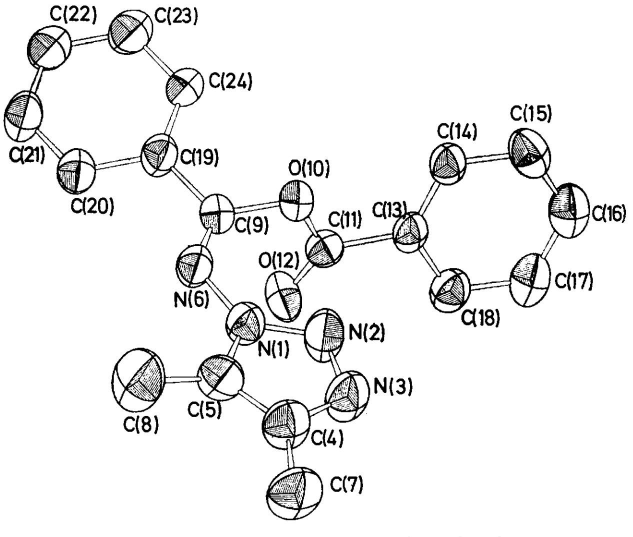

FIGURE 3 The molecular structure of molecule (10). The vibrational ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted

Some very short intramolecular contacts are found, resulting in a very closely packed molecule. The distance between O(10) and N(2) of the triazole ring is 2·71 Å, that between O(10) and C(24) of the first benzene ring is 2·81 Å, and that between O(10) and C(14) of the other benzene ring is 2·77 Å. Other relevant short intramolecular contacts are between the carbonyl oxygen O(12) and the aromatic carbon C(18) of the adjacent benzene ring (2·86 Å), and between the N(6) and the aromatic carbon C(20) of the other benzene ring (2·84 Å).

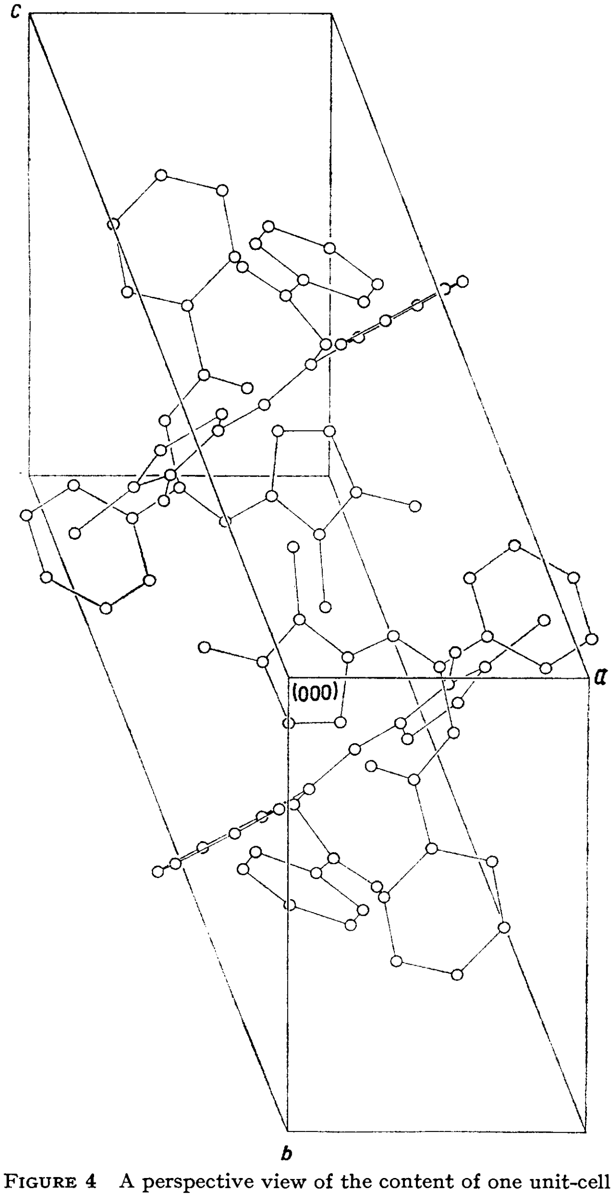

FIGURE 4 A perspective view of the content of one unit-cell of the crystal of compound (10)

The crystal packing of the molecules is shown in Figure 4.

General Conclusions.—The *X*-ray evidence clearly demonstrates that the imidic acid structure (10) is correct. Most of the chemical and spectroscopic evidence is explained by this structure equally or better than by the *N*-imide structure (9); this applies also to evidence presented elsewhere, particularly by Alexandrou.[9] Additionally, recent work has shown that *O*-acyl imidic acids are stable compounds, particularly when the nitrogen atom carries an electron-withdrawing substituent.[29]

EXPERIMENTAL

Biacetyl Bisphenylsulphonylhydrazone (14).—Biacetyl was converted into (14) by the general procedure of Bamford and Stevens.[30] The *product* formed prisms, m.p. 198—199° (from dimethylformamide) (Found: C, 48·2; H, 4·3; N, 14·3. $C_{16}H_{18}N_4O_4S_2$ requires C, 48·6; H, 4·7; N, 14·2%).

Heating the bis-sulphonylhydrazone (14) (0·2 g) with potassium hydroxide in ethylene glycol (10%; 2 ml) for 5 min at 150°, followed by dilution with water and neutralisation (HCl) yielded 4,5-*dimethyl*-1-*phenylsulphonylamino*-1,2,3-*triazole* (0·09 g, 70%), m.p. 160—161·5° (from water) (Found: N, 22·1. $C_{10}H_{12}N_4O_2S$ requires N, 22·2%).

2,3-*Bis*(*phenylsulphonylazo*)*but*-2-*ene* (15).—The osazone (14) (1 g) in ethanol (5 ml) and aqueous 10% sodium hydroxide (2·5 ml) was added dropwise, with stirring, to aqueous potassium ferricyanide (2·5 g in 10 ml) at 0°. An orange precipitate formed, which after 1 h was filtered off and washed with water. The residue was dried and dissolved in cold chloroform, and the red *azo-compound*, m.p. 91° (explosive decomposition), crystallised out on addition of ether (Found: N, 14·2. $C_{16}H_{16}N_4O_4S_2$ requires N, 14·3%).

Attempted Alternative Synthesis of the O-*Acyl Imidic Acid* (10).—1-Benzoylamino-4,5-dimethyl-1,2,3-triazole[8] (16) (2 g) was heated under reflux in toluene with excess of thionyl chloride. After removal of solvent, the crystalline residue, presumably the *hydrochloride* (17) [$\nu_{max.}$ (Nujol) 2290br and 1900br cm^{-1}], gave on treatment with sodium benzoate in dimethylformamide, followed by addition of water, an oily product [$\nu_{max.}$ (film) 1790 and 1730 cm^{-1}], clearly not identical with the imidic acid derivative [' enol benzoate ' (10); $\nu_{max.}$ (Nujol) 1750 and 1639 cm^{-1}].[8]

Attempted Preparation of Biacetyl Monobenzoylhydrazone Monophenylhydrazone (19).—When heated under reflux, equimolar quantities of biacetyl monophenylhydrazone[31] and benzohydrazide[32] in ethanol yielded a yellow precipitate. This (1·5 g) in ethanol (25 ml) was treated with aqueous sodium hydroxide (4·5 ml) and potassium ferricyanide (5·5 g in 20 ml H_2O). After 1 h stirring, and dilution with water, the red-violet azo-compound (21) was filtered off, and crystallised from ethanol as needles, m.p. 150—151° (lit.,[17] 169°) (Found: C, 72·7; H, 6·2; N, 21·2. Calc. for $C_{16}H_{16}N_4$: C, 72·7; H, 6·1; N, 21·2%). The expected co-product (10) was not isolated, but the smell of ethyl benzoate, a logical product of its decomposition in ethanol, was detected.

The bisazo-compound (21) was heated at 190° for 2—3 min, to yield a yellow *isomer*, m.p. 230—233° (decomp.) (Found: N, 21·0%).

1-(α-*Benzoyloxybenzylideneamino*)-4(5?)-*methyl*-1,2,3-*triazole* (23).—Prepared by the method of Stolle,[20] this had m.p. 123—124° (lit.,[20] 124°); τ (C_6H_6) 8·1 (d, *J* 0·8 Hz, CH_3). Thermal rearrangement (100°; 12 h) formed the 1-dibenzoylamino-compound (not isolated); τ (C_6H_6) 8·3 (d, *J* 0·8 Hz, CH_3).

By standard methods (HgO–I_2 oxidation in ether)[20] the following bisacylhydrazones were oxidised: pentane-2,3-dione bisbenzoylhydrazone (m.p. 239—240°) [yielding two isomeric O-*acyl*-N-*triazolylimidic acids*, one isolated, m.p. 135—136° (Found: C, 68·2; H, 5·6; N, 17·0. $C_{19}H_{18}N_4O_2$ requires C, 68·2; H, 5·6; N, 16·8%); τ (C_6H_6) 8·0 (CH_3), the other, τ (C_6H_6) 8·1 (CH_3), not], *biacetyl bis*-p-*chlorobenzoylhydrazone*, m.p. 306° (decomp.) (Found: C, 55·4; H, 4·0. $C_{18}H_{16}Cl_2N_4O_2$ requires C, 55·2; H, 4·1%) [yielding the respective imidic acid derivative, m.p. 155—156°], *biacetyl bis*-m-*chlorobenzoylhydrazone*, m.p. 286° (Found: C, 55·5; H, 4·4%) [yielding the m-*chlorobenzimidic acid derivative*, m.p. 117—118° (Found: C, 55·4; H, 4·0. $C_{18}H_{14}Cl_2N_4O_2$ requires C, 55·5; H, 3·6%)], *biacetyl bis*-p-*bromobenzoylhydrazone*, m.p. 310° (decomp.) (Found: C, 45·6; H, 3·5. $C_{18}H_{16}Br_2N_4O_2$ requires C, 45·0; H, 3·3%) [yielding the p-*bromobenzimidic acid derivative*, m.p. 164·5—165·5° (Found: C, 45·3; H, 2·9; N, 12·0. $C_{18}H_{14}Br_2N_4O_2$ requires C, 45·2; H, 2·9; N, 11·7%)], and *biacetyl bis*-m-*bromobenzoylhydrazone*, m.p. 245° (Found: C, 45·0; H, 3·3%) [yielding the m-*bromobenzimidic acid derivative*, m.p. 127° (Found: C, 45·2; H, 3·1; N, 11·7%)]. The last four oxidation products crystallised from a number of solvents as extremely fine fragile white needles.

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