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THE STRUCTURE OF SUGAR OSAZONES

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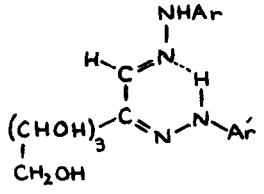
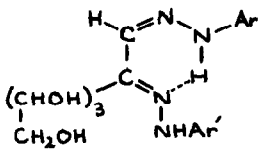
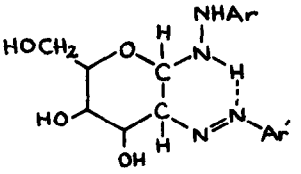
Recently, Blair and Roberts[1] have published evidence in favour of the cyclic structure (II) for the sugar osazones, rather than the generally accepted acyclic structures (I)[2,3].



Ia



Ib



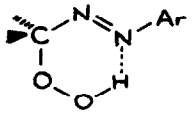
II

Their evidence is drawn from infrared and ultraviolet spectroscopy and from various reactions of the osazones which are said to be inconsistent with the chelate bis-hydrazone structures (Ia) and (Ib). Their paper[1] contains several anomalies.

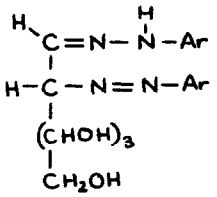
Firstly, the UV-visible spectra of the osazones are inconsistent with structure (II), which contains an isolated phenylazo chromophore and an isolated (2-phenylhydrazine)-chromophore. In support of their assignment, the authors[1] quote ultraviolet data from Brede and his co-workers[4] and from Cook, et. al[5]. which is claimed to support their contention that structure (II) should be associated with a strong absorption band ($\varepsilon \triangleq 20{,}000$) in the 390-410 nm region such as is shown by osazones. This is incorrect; these data[4,5] refer only to diarylazo compounds such as 4-(dimethylamino)-azobenzene (λ_{max} 410 nm, ε_{max} 28,300)[4] which contain quite different chromophores from that required by formula (II). The absorption spectra of phenylazoalkanes

are well known[6,7] to be characterised by a $\pi - \pi^*$ transition ($\varepsilon \sim 15{,}000$) below 300 nm and a weak $n - \pi^*$ transition ($\varepsilon > 200$) in the 400 nm region. This combination of bands is characteristic and quite unlike that of osazones. The phenylhydrazino chromophore is essentially transparent above 300 nm.

It might be argued that hydrogen bonding in structure (II) might influence the spectrum of the azo group, but although hydrogen bonding may cause spectroscopic changes, these are usually small, as pointed out by Blair and Roberts[1]. The nearest analogy to such a hydrogen bond is that found in the phenylazo-hydroperoxides (III), which are hydrogen-bonded in non-polar solvents[7b,8]. Their absorption spectra closely resemble those of unsubstituted phenylazoalkanes[6-9] (2-hydroperoxy-2-phenylazopropane[6], λ_{max} 266.5 and 411 nm, ε 9560 and 134).



III



IV

It is also claimed by a roundabout analogy[1] that the spectrum of glucose (p-nitrophenyl)osazone (λ_{max} 448 nm, ε 31,300) is consistent with the chromophore $-N{=}N-C_6H_4-NO_2$ as required by formula (II). In fact one compound, 3§-hydroperoxy-3§-(p-nitro-phenylazo) cholestane, is known containing this chromophore[7a] and its spectrum is of the typical azoalkane type (λ_{max} 284 and 425 nm; ε 20,300 and 264) with some bathochromic shift of the $n - \pi^*$ band attributable to the nitro group.

The authors[1] also fail to mention that the X-ray structure of xylose (p-bromophenyl)-osazone shows it to be acyclic in the solid state[10]. It has a typical osazone absorption spectrum (λ_{max} 399 nm, ε 25,300). The physical evidence in favour of structure (II) therefore rests only on infrared absorption data[1], which in the light of the

difficulties experienced by other workers in making definite assignments to -N=N- absorptions[11], must be considered equivocal in the absence of supporting evidence[12].

Structure (II) is by itself insufficient to explain the reactions of osazones such as tetra-O-acylation[1] and the formazan reaction (C=N-NH- group required[9]) and an equilibrium in solution with an "acyclic form"[1] must be postulated. The structure of this form was not specified[1], but it can only be the phenylazo-hydrazone (IV) or the "normal" forms (I).

Structure (IV) is also extremely improbable for the following reasons.

(1) Its UV-visible spectrum would again not correspond to that of an osazone.

(2) Its nmr spectrum would not agree with those published (two NH protons[3a]) unless a large amount of the cyclic form (II) were assumed to be in equilibrium with a small amount of the acyclic form (IV). In this case it is not possible to explain the C_1-H resonance of osazones at 2-3τ [3a,13].

(3) Present knowledge[6,9] of the essentially irreversible tautomerism of arylazoalkanes to arylhydrazones under the usual conditions predicts the thermodynamic instability of structure (IV) relative to the "normal" osazone structures (I). Tautomerism of (I) into (IV) is even less favoured than that of a simple phenylhydrazone since conjugation of the two C=N π bonds must increase the stability of the hydrazone form, and further stabilization associated with "quasi-aromaticity" of the osazone chelate structure is also a probability[3c].

Furthermore, no mechanism of osazone formation is conceivable which would lead directly to an azoalkane. The "normal" osazone (I) must be the first product, whatever the detailed mechanism[15], and to form either azo structure (II) or (IV) it must undergo an arylhydrazone→ arylazo rearrangement with simultaneous deconjugation of the double bonds.

Alternatively, an equilibrium in solution between cyclic form (II) and a preponderance of bis-hydrazone forms (Ia) and (Ib), although

it would explain the UV and nmr spectra, is similarly untenable, since using Blair and Roberts[1] explanation of the acetylation of the osazones it is impossible to devise a scheme which would explain the formation of both tetra- and penta-acetyl derivatives.

It is thus clear that the proposed[1] structure (II) must be rejected on a variety of evidence.

REFERENCES.

1. H.S. Blair and G.A.F. Roberts, J. Chem. Soc.(C), 1969, 2357.

2. L.F. Fieser and M. Fieser, "Organic Chemistry", D.C.Heath and Co., Boston, 1944, p.351.

3. (a) L. Mester, E. Moczar and J. Parello, J. Amer. Chem. Soc., 1965, 87, 596. (b) H. El Khadem, M.L. Wolfrom and D. Horton, J. Org. Chem., 1965, 30, 838. (c) L. Mester, G. Vass, A. Stephen and J. Parello, Tetrahedron Letters, 1968, 4053.

4. W.R. Brode, J.H. Gould and G.M. Wyman, J. Amer. Chem. Soc., 1952, 74, 4641; 1953, 75, 1856; M.N. Inscoe, J.H. Gould and W.R. Brode, ibid., 1959, 81, 5634.

5. A.H. Cook, D.G. Jones and J.B. Polya, J. Chem. Soc. 1939, 1315.

6. A.J. Bellamy and R.D. Guthrie, J. Chem. Soc. 1965, 2788.

7. J. Buckingham and R.D. Guthrie, (a) J. Chem. Soc. (C), 1968, 1445. (b) ibid., 1969, 1939.

8. R. Criegee and G. Lohous, Chem. Ber., 1951, 84, 219.

9. J. Buckingham, Quart. Revs., 1969, 23, 37.

10. K. Bjåmer, S. Dahm, S. Furberg and C.S. Petersen, Acta. Chem. Scand., 1963, 17, 559.

11. See refs. 15 and 20-22 in ref. 1.

12. 1-phenylazo-2-(2-phenylhydrazino)-cyclohexane has been postulated (ref. 14) as an intermediate in the reduction of 1,2-bisphenylazocyclohexane and is thought capable of ring-chain tautomerism to yield adipaldehyde bis-phenylhydrazone. Such a process occurring to structure (II) would result in loss of C_1.

13. H-C=N-N-Ph. appears at about 6τ (Refs. 6 and 14).

14. A.J. Bellamy, R.D. Guthrie and G.J.F. Chittenden, J.Chem. Soc., 1966, 1989.

15. H. Simon and W. Moldenhauer, Chem. Ber., 1969, 102, 1191.