# 1,3′: 1,3′-Diepoxy-3,3′-diphenyl-2,2′-bi-indolinyl, a Product from the Reaction of Phenylacetylene with Nitrosobenzene

By J. IBALL, W. D. S. MOTHERWELL, J. J. S. POLLOCK, and J. M. TEDDER*

(*Chemistry Department, The University, Dundee, Scotland*)

WHEN a solution of phenylacetylene and nitrosobenzene in dry carbon tetrachloride is boiled under reflux for six hours, a crystalline product can be isolated in *ca.* 8% yield; m.p. 202—204°, i.r. (KCl disc) $\nu_{max}$ 1600m, 1470s, 1450s, 975s, 760vs, split, 708s br cm.$^{-1}$; u.v. ($CHCl_3$ solution) end absorption only (the compound is insoluble in ethanol); n.m.r. ($CHCl_3$ solution) 12·4—3·2 (aromatic protons *ca.* 18), $\tau$ 4·65 (sh, s, 1 proton); combustion analysis C, 14·11; H, 10·23; N, 1·00; O, 1·03; mass spectrum peaks at *m/e* 416, 400, 399, 209 vs, 208, 194, 193, 192, 180, 165, 152, 105, 104, 102, 77. The product is insoluble in ethanol, sparingly soluble in acetone, benzene, and carbon tetrachloride, and moderately soluble in chloroform. The compound shows no chemical evidence for unsaturation and is resistant to attack by normal reagents including sodium methoxide in

refluxing methanol. It is decomposed by strong acids to unidentified products and although unaffected by hydrogen and a catalyst (Ni or Pd/C) at atmospheric pressure, high pressure hydrogenation (Ni at 100°, 60 atmos.) caused decomposition to unstable products.

To establish the molecular structure of the crystalline product an *X*-ray diffraction study was carried out. The crystals are monoclinic with $a = 23{\cdot}85$, $b = 7{\cdot}90$, $c = 13{\cdot}07$ Å, $\beta = 120{\cdot}4°$, and the systematic absences were $hkl$ when $h + k = 2n + 1$ and $h0l$ when $h$ or $l$ is odd. The space group is therefore $Cc$, $C2/c$, or $C2/n$. The observed density was 1·309 g./cm.$^3$ and if we assume a molecular weight of 208 this gives 8 molecules per unit cell suggesting that the space group is not $Cc$. This was confirmed by statistical analysis of the diffraction data which indicated clearly that the crystals were centrosymmetric. Three-dimensional data with Cu-$K_\alpha$ radiation were collected on a Wooster 4-circle diffractometer and the strong reflections were measured with Mo-$K_\alpha$ radiation on a Hilger and Watts linear diffractometer. Some 2100 independent reflections were observed and the signs of 231 of these were determined by the method of symbolic addition.[1]

A three-dimensional *E*-map was computed and the 16 highest peaks revealed the structure of a dome-shaped dimeric molecule with a 2-fold axis coincident with the 2-fold axis of space group $C2/c$. The Figure represents the chemical formula. The molecular weight is 416 and therefore there are 4 molecules per unit cell.

The co-ordinates of the peaks were determined from the *E*-map and used for a structure-factor calculation with all the 2100 independent reflections. This gave an *R*-factor of 40% and 4 cycles of least-squares refinement with isotropic thermal parameters reduced *R* to 13·3%. The bond-lengths and bond-angles are as expected from the Figure.

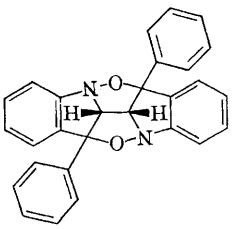


FIGURE. $C_{28}H_{20}O_2N_2$

In retrospect the i.r., u.v., n.m.r. and mass spectrometry data are all consistent with the molecular structure of the Figure.

The refinement of the *X*-ray crystal structure is continuing and the mechanism of the reaction is being studied.

We thank the Computing Laboratory of the University of St. Andrews for the use of the IBM 1620 computer. One of us (J.I.) thanks the British Empire Cancer Campaign for Research for support.

(*Received, February 2nd*, 1968; *Com.* 133.)

[1] J. Karle and I. Karle, "Computing Methods in Crystallography," ed. J. Rollett, Pergamon Press, 1965.