[2 + 2] Cycloaddition of Two C=N Double Bonds. First Structural Evidence for Head-to-tail Photodimerization in the 2-Phenylbenzoxazole Series

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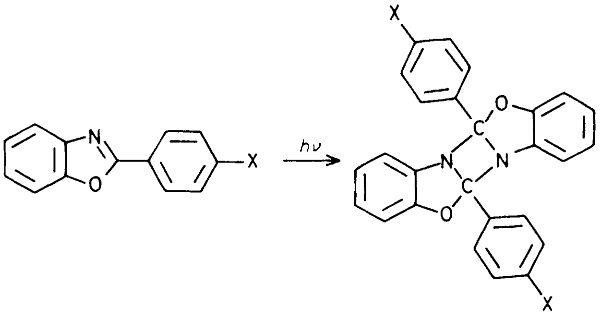
Irradiation of 2-(4-fluorophenyl)benzoxazole in a two-phase medium leads to crystals of the [2 + 2] photoadduct; the head-to-tail structure of this dimer has been demonstrated by an *X*-ray study.

While [2 + 2] cycloadditions of C=C double bonds are well known, photodimerizations involving C=N double bonds have rarely been observed, only three cases so far having been reported.[1—3] This may be due either to the low reactivity of the C=N group or to the low stability of the resulting diazetidines. One of the first examples of such a reaction was the photodimerization of 2-phenylbenzoxazole. Unstable in solution, the photodimer may revert thermally to the starting material thus releasing 116 kJ/mol. This property allowed us to propose this monomer $\rightleftarrows$ dimer reversible reaction as an attractive system for light energy conversion.

On the basis of analytical data and spectroscopic studies the photodimers of 2-phenylbenzoxazole derivatives[4] were shown to result from a cycloaddition reaction involving the C=N bonds. The ^{13}C n.m.r. data suggested a 1,3-diazetidine structure, but it was not certain whether it was a head-to-tail or head-to-head process, as was also the case for the two other known examples. It was difficult to determine the regioselectivity of the photodimerization because of the instability of the photodimers and the failure to get crystals of convenient size for *X*-ray analysis.

However, an unusual irradiation technique in a two-phase medium has allowed us to obtain photodimers of 2-phenylbenzoxazole derivatives in higher yield and better crystalline form than in homogeneous media. An oxygen-free saturated solution of the benzoxazole in n-hexane (4 cm^3) was poured into a Pyrex test-tube containing distilled water (4 cm^3). During irradiation at 300 nm, the photoproducts appeared as a film at the interface between the two phases. The photodimerization quantum yields for the 2-(4-X-substituted phenyl)benzoxazole ($\phi = 8 \times 10^{-2}$, 2×10^{-2}, and 1.4×10^{-3} respectively for X = H, Cl, and F in n-hexane) increased up to fifty fold in this heterogeneous medium ($\phi = 3.5 \times 10^{-1}$, 9×10^{-2}, and 7.7×10^{-2} respectively). Furthermore, the 4-methoxy derivative, which did not dimerize in the homogeneous medium gave rise to a photodimer† under these conditions ($\phi = 10^{-3}$). An *X*-ray study was carried out on the dimer of the fluoro derivative, whose crystals, although small, were of the most convenient size and form.‡



This *X*-ray analysis indicated that the photodimerization selectively led to the head-to-tail diazetidine (Figure 1). The space group requires that the molecule is centrosymmetric, and so the diazetidine ring is planar, which generally imposes a larger constraint than the folded shape. This feature could be either a consequence of the crystal packing effects or a characteristic of the isolated molecule due to the simultaneous incorporation of the two diazetidine C–N bonds in the fused rings. Molecular mechanics calculations show that the centrosymmetry and thus the planarity of the four-membered ring are an intrinsic property of the molecule in the free state.§

The unit cell contains two crystallographically independent

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† Satisfactory elemental analyses were obtained. The i.r. spectrum of the dimer shows the absence of the characteristic bands of the monomer C=N (1618 cm^{-1}) and N=C—O (1503 cm^{-1}), thus indicating the participation of the C=N double bond in the reaction. The decomposition behaviour is identical to that of the other dimers.

‡ *Crystal data:* $C_{26}H_{16}F_2N_2O_2$, $M = 426.43$, triclinic, space group $P\bar{1}$, $a = 6.737$, $b = 11.722$, $c = 13.303$ Å, $\alpha = 100.93$, $\beta = 99.9$, $\gamma = 94.43°$, $U = 1009.6$ Å^3, $F(000) = 440.0$, $Z = 2$, $D_m = 1.40\ (\pm 0.1)$, $D_c = 1.40$ g cm^{-3}, μ(Mo-K_α) = 0.96 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\bar{\lambda} = 0.71073$ Å) to $\theta = 30°$. The crystal was a near-regular parallelepiped whose largest dimension was $\leqslant 0.15$ mm. Because of the low absorption coefficient these dimensions were not the most favourable, but it was the only sample of sufficient quality. Measurements around the scattering vector for ten reflections chosen in different Bragg domains did not show significant intensity variation. Therefore, no absorption corrections were applied. Lorentz–polarization corrections have been performed. Control reflection intensities, measured every hour, showed a near-isotropic, continuous non-linear decrease to 18% of the initial values. There was no orientation change nor modification of the unit cell, however because of the interest of the compound, we proceeded with refinement after isotropic degradation correction as no other crystal was available for the measurement of another data set. Calculations were performed on a VAX 11/730 computer using the SDP[5] and SHELX programs. The structure was solved by direct methods (MULTAN). Blocked-cascade least-square refinement and difference Fourier syntheses located all non-hydrogen atoms. In order to limit the errors introduced by the degradation corrections, 935 out of 5904 recorded unique reflections were used [$I \geqslant 3\sigma(I)$]. The hydrogen atoms were located from a ΔF map and their positions were compared with those calculated theoretically. The *R* factor of 0.109 (R_w 0.116) is not very satisfactory but can be explained by the difficulties encountered in the data collection. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Calculations performed on molecules I and II (in the crystal) using the Newton–Raphson technique for minimization of the steric energy in the Allinger force field (Program MM2, 1977) have shown that (i) the structure of molecule I is very close to the lowest energy conformation calculated for it *'in vacuo;'* (ii) molecule II diverges from the calculated conformation in the N(51)–C(51′) and N(51′)–C(51) bond lengths, whose stretching causes a 16.7 kcal mol^{-1} (1 kcal = 4.184 kJ) energy increase. It thus cannot be a conformer and, when allowed to relax, evolves without any barrier encounter towards the calculated conformation.

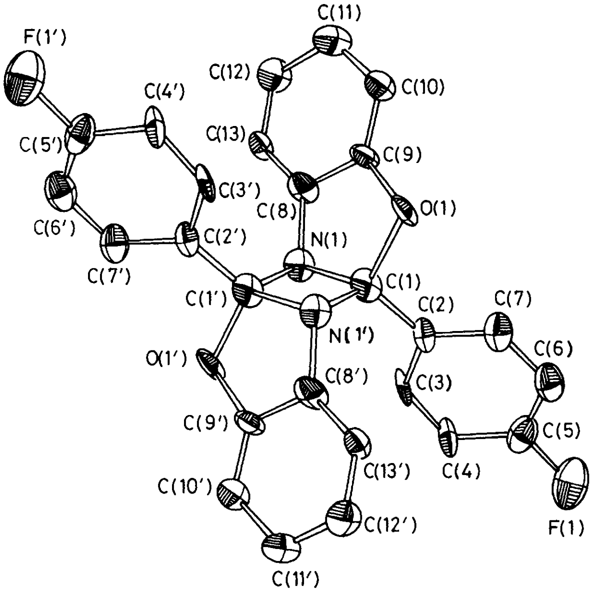

Figure 1. Perspective view (20% probability ellipsoids) and labelling scheme for the 2-(4-fluorophenyl)benzoxazole dimer (molecule). Numbering of atoms in molecule I starts at 1, and that of molecule II at 51. Selected bond lengths and angles (e.s.d.s. for angles are 1°): O(1)–C(1) 1.499(14); O(1)–C(9) 1.403(14); F(1)–C(5) 1.38(2); N(1)–C(1) 1.506(13); N(1)–C(1′) 1.51(2); N(1)–C(8) 1.423(15); C(1)–C(2) 1.50(2); C(8)–C(9) 1.386(15); O(51)–C(51) 1.42(2); O(51)–C(59) 1.446(15); N(51)–C(51) 1.482(14); N(51)–C(58) 1.45(2); C(51)–C(52) 1.41(2); N(51)–C(51′) 1.67(2) Å; C(1)–O(1)–C(9) 108; C(1′)–N(1)–C(1) 87; C(1)–N(1)–C(8) 107; C(1′)–N(1)–C(8) 115; O(1)–C(1)–N(1) 104; O(1)–C(1)–N(1′) 112; O(1)–C(1)–C(2) 107; N(1)–C(1)–N(1′) 93; N(1)–C(1)–C(2) 117; N(1′)–C(1)–C(2) 123; C(1)–C(2)–C(3) 121; C(1)–C(2)–C(7) 120; N(1)–C(8)–C(9) 110; N(1)–C(8)–C(13) 131; C(9)–C(8)–C(13) 118; O(1)–C(9)–C(8) 110; O(1)–C(9)–C(10) 125; C(8)–C(9)–C(10) 125; C(51)–O(51)—C(59) 107; C(51)–N(51)–C(51′) 92; C(51)–N(51)–C(58) 105; C(51′)–N(51)–C(58) 116; O(51)–C(51)–N(51) 108; O(51)–C(51)–N(51′) 107; O(51)–C(51)–C(52) 112; N(51)–C(51)–N(51′) 88; N(51)–C(51)–C(52) 121; N(51′)–C(51)–C(52) 117°.

molecules (Figure 2), each with a centre of symmetry, at 0,0,1/2 (for molecule I) and 1/2,1/2,0 (for molecule II). The two fused rings of the benzoxazole moiety remain coplanar. Angles between the normals to the diazetidine plane and to the benzoxazole plane in molecules I and II are respectively 66.4 and 66.7°.

As for bond distances, because of the large uncertainties due to decomposition, the differences between the two molecules are not significant for most bonds. If we fix the significance threshold at 3 e.s.d. almost all related bond lengths are equal. There is however clearly one exception: the N(1)–C(1′) bond length [1.51(2) Å] in molecule I is shorter than the corresponding distance N(51)–C(51′) [1.67(2) Å] in molecule II. In addition while the two interatomic distances N(1)–N(1′) and N(51)–N(51′) are almost identical [2.19(2) and 2.20(3) Å respectively] the C(51)–C(51′) distance [2.28(3) Å] is larger than C(1)–C(1′) [2.07(3) Å] in accordance with the increase of the aforementioned C–N bonds lengths. The angles are not significantly different. In summary, the diazetidine ring in molecule I has a rhomboid geometry and in molecule II it is a parallelogram.

Two hypotheses may be considered to explain the significant increase by 11% of the length of the C–N bonds which link the benzoxazoles moieties. In the first, the two types of molecule I and II could be two conformers resulting from distortion due to packing forces. However, the large increase in the C-N bond length implies a considerable increase in the strain energy as shown by molecular mechanics calculations. In the second, the difference could result from *X*-ray degradation, the geometry of molecule II depicting an average view of the molecule on the decomposition pathway. Both molecules are similarly sensitive but in the case of molecule II its surroundings would probably provide more room for separation into the monomers. Such a topological effect is well known for the inverse reaction, the dimerization of cinnamic acid,[6] which also leads to the formation of a four-membered ring.

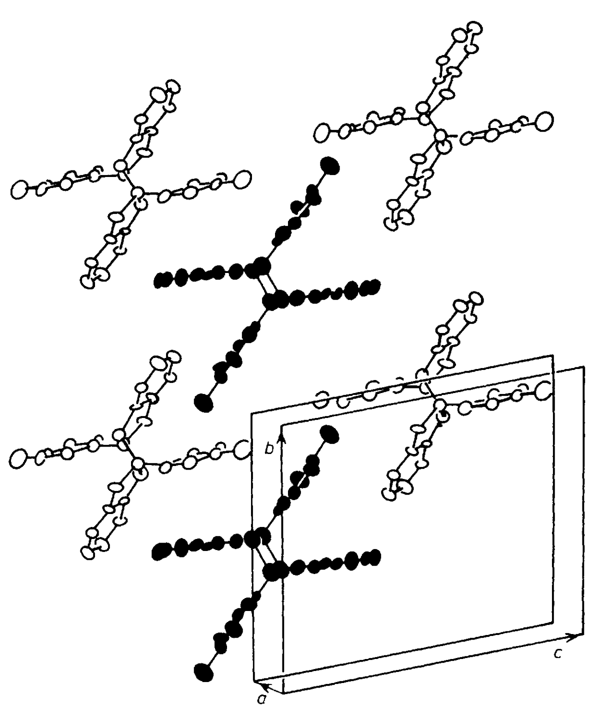

Figure 2. Perspective view showing the disposition in the unit cell of molecules I (unshaded) and II (shaded).

The differences between the two types of molecule could also be due to the inclusion in the lattice of some monomer, although the spectroscopic characteristics of the latter were not observed. Furthermore, the experimental and calculated densities would not be in good agreement and the site occupation factors should be 1/2, which obviously is not the case.

Discrimination between these different points of view would require considerable further experimentation. Low temperature measurements are under way in order to reduce decomposition as well as the high thermal motion. The *X*-ray analysis, in providing structural proof for the head-to-tail diazetidine, thus gives a definitive answer to the question of the regioselectivity of this photodimerization.

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