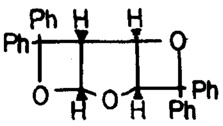
Tetrahedron Letters No.42, pp. 4119-4122, 1967. Pergamon Press Ltd. Printed in Great Britain.

ON THE STRUCTURE OF THE 2:1-ADDUCT OF BENZOPHENONE AND FURAN

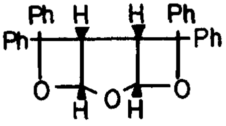
Susumu Toki and Hiroshi Sakurai
The Institute of Scientific and Industrial Research
Osaka University, Osaka, Japan

(Received in Japan 20 June 1967)

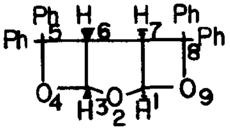
Ogata et al., reported that the photoaddition of benzophenone to furan gave two isomeric 2:1-adducts (I, II) based on the determination of dipole moment (1). On the other hand, we deduced that the symmetrical adduct was preferred III to II from a consideration of the NMR-spectrum and the steric requirement (2). Recently, Leitich (3) and Evanega et al., (4) independently reconsidered the dipolemoment data and the NMR-spectrum, and assigned III rather than II to the symmetrical adduct. Since one generally can not precisely determine and calculate dipole moment, there is the possibility of misassignment in the case of a slight difference between the dipole moments of compounds. Therefore, in order to determine which structure is correct we have investigated the structure by means of the single-crystal X-ray method in addition to the indirect measurements (UV- and NMR-spectra).



I



II



III

The crystal of the symmetrical adduct was obtained from benzene solution, of which physical properties (m.p. and NMR-spectrum) were in agreement with the results of Ogata and coworkers. The crystal is monoclinic with the cell dimensions, a=14.5, b=6.5, c=11.6Å, and β=100°. The possible space groups are *I2/m*, *Im*, and *I2* based on the systematic absences. The unit cell contains two molecules on the basis of the observed density 1.28g.cm^{-3} of the crystal (calculated density $1.34 g\cdot cm^{-3}$). In view of the number of molecules in the unit cell and the requirement of space groups, the molecule itself must have the point group 2/m, m, or 2 according to the space group of I2/m, Im, or I2, respectively. As the molecule has the point group m for the syn-configuration and the point group 2 for the anti-configuration, I2/m is ruled out. Let us assume that the molecule has the syn-structure. The space group must be Im, and the distance of equivalent mirror planes is equal to the b-length, 6.5Å. But it is impossible to pack the molecule with the length of about 12Å perpendicular to the mirror. Thus the space group of the crystal can not be Im. Only possible space group, therefpre, is I2, and the molecule must be the anti-structure in the crystal. Although the phase differs in the measurements of dipole moment and X-ray analysis, a more thermodynamically stable structure is generally preferred in the solution to in the crystal, thus in the liquid the structure may be populated in the anti-structure.

The result is in agreement with the prediction according to UV- and NMR-spectra. The absorption curve of the adduct (λ_{max} (ε) 258.5(1000), 264 mμ (740) in ethanol) is almost identical with the absorptions of the 1:1-adduct(IV) (λ_{max} (ε) 258.5(520), 264 mμ(390) in ethanol) and diphenylmethane (λ_{max} (ε) 260(490), 268.5 mμ(420) in ethanol) in double concentration above 250 mμ, where double bond of IV does not participate in UV-spectrum. This observation shows *no interaction between non-bonded phenyl groups, that is, the structure is the* anti-structure; *since if the structure is the syn-form, in which the phenyl* groups are very close to each other, in fact, they collide against the other in the molecular model, the interaction of non-bonded aromatic rings as observed in cyclophanes and triptycenes (5) should lead to the longer wave length shift and higher absorption coefficient in UV-spectrum.

Not only the absence of an observable coupling between proton 6 and 7 in the symmetrical adduct, as indicated before (3, 4), but also the chemical shift of proton 6 (or 7) leads to assign the anti-configuration to the adduct.

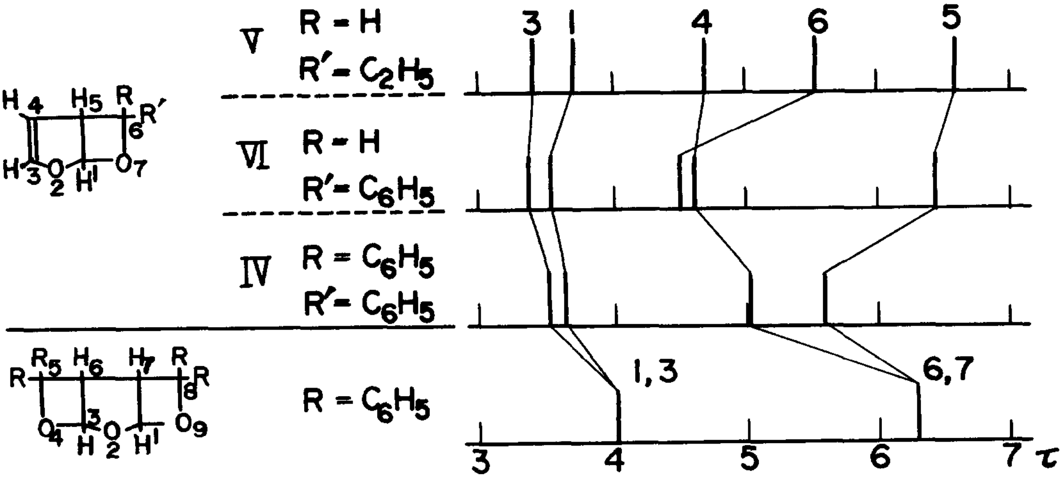


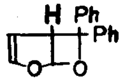
Fig.1. Chemical shifts for protons of oxetanes in chloroform-d

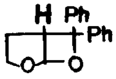
Chemical shifts of substituted oxetanes in chloroform-d (6) are presented in Fig.1. Substitution of ethyl group (V) to phenyl (VI) almost does not change in the chemical shifts of protons. The introduction of one more phenyl group (IV) leads proton 5 to lower field, but proton 4 to higher field shifts. The abnormal shifts are the results of diamagnetic and paramagnetic shieldings by the second phenyl group. The similarly abnormal higher shift (6.29τ) was observed in the proton 6 (or 7) in the symmetrical adduct. Its shift is more than that due to the conversion of allyl to methine proton*. The proton 6 in III lies right above one phenyl group, whereas in II does not. Therefore the higher shift fits for the anti-form, but does not for the syn-form.

The above data leave no doubt that the symmetrical 2:1-adduct has the anti-configuration (III).

---

*The chemical shifts of model compounds in CCl_4 (7)

 5.70τ

 6.12τ 0.42ppm

Acknowledgement. The authors are greatly indebted to Professor N. Morimoto in this Research Institute for the X-ray analysis and helpful discussion.

REFERENCES

1) M.Ogata, H.Watanabe and H.Kano, *Tetrahedron Letters*, No. 6, 533 (1967).

2) Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967.

3) J.Leitich, *Tetrahedron Letters*, No. 20, 1937 (1967).

4) G.R.Evanega and E.B.Whipple, *ibid.*, No. 23, 2163 (1967).

5) H.H.Jaffe and M.Orchin, "*Theory and Applications of Ultraviolet Spectroscopy*", John Wiley & Sons, Inc., 1962, p443-8.

6) S.Toki, K.Shima and H.Sakurai, *Bull.Chem.Soc.Japan*, **38**,760 (1965).

7) D.Gagmaire and E.Payo-Subiza, *Bull.Soc.Chim. France*, 1963, 2623.