09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-36 *STRUCTURE AND FLEXIBILITY OF MODEL SYSTEMS FOR THE PLANT FIGMENT PHOTOCHEMISTRY*;

By Christopher Rosky. Institut für physikalische Chemie, Universität Graz, A-8010 Graz, Austria.

Phytochrome is the photoreceptor in higher plants responsible for photomorphogenesis. There exists considerable evidence that 1,6 isomerism about one of the exocyclic double bonds plays an important role in its function.

Crystal structures of several model systems for phytochrome were determined, including systems with the complete phytochrome chromophore and pairs of E/Z isomers (about the 4-5 bond) for an N-methylated dihydroprotoxanthone and for a phytochrome analog with a carbonyl group in position 3. All structures were determined at low temperature and they yield an accurate structural characterization of this biologically important system.


09.2-37 COUPLING PRODUCTS OF DIAZONIUM SALTS FOR TETRAHYDRO-4,8-METHANO-1,5-NAPHTHOQUINONE.

By C.-P. Kaerlein, A. Gieren and A. Betz, Max-Planck-Institut f. Biochemie, Abt. Strukturforschung I. 8033 Martinsried, FRG.

With respect to the 1,6-methano[10]annulene derivatives 1 and 2, valence tautomeric forms, the cycloheptatriene forms 1g, 1h and the norcaradiene forms 1e, 1f as well as the tautomeric hydrozonic forms (1g, 1h) in comparison to the azo forms (1j, 1k) have to be discussed. Compound 1 with respect to the molecular geometry is a positional isomer of 1 with a para-arrangement of the semicyclic double bonds in contrast to an ortho one in 1,14-hydrozonic spectra indicated a norcaradiene form for 1 and a cycloheptatriene form for 2. Also for 2 a norcaradiene (3b) and a cycloheptatriene form (3g) have to be considered. An X-ray structure analysis (R. Neidlein, C.-N. Radke, E. Hädicker, and A. Gieren, Chem. Ber. (1983) 116, 2881) revealed 3g to exist in a cycloheptatriene form and an open hydrozonic tautomer. Both the molecular geometry and, particularly, the 1,6-C-C distance of 2.28 Å indicate a very small contribution of a norcaradiene tautomeric structure of type 1g. Recently the cycloheptatriene form and the hydrozonic tautomer (3g) were found in the case of 1 too. In this case, however, the 1,6-C-C distance of 2.23 Å is significantly shorter indicating a stronger contribution of the norcaradiene tautomeric structure 1g compared with the analogous form in the case of 2.

Furthermore, the C-C-C angle of the CH₂ bridge is ca. 5° smaller. The configurations of 1 and 2 are stabilized by hydrogen bonds. The formation of different hydrogen bonds in 1 and 2 gives rise to configurational differences between 1 and 2 with respect to the C-N bond. The differences between the positional isomers of the 1,6-methano[10]annulenes (with 1 being orthoquinoid and 2 parquinoid) are associated with specific alternations of the bond lengths. Compared with 1 and 2, compound 3 has a naphtaloid-naphthoquinone-like structure and thus exhibits an 1,6-C-C bond giving rise to the formation of a cyclopropane ring. The bonding features are best described by the canonical formula 3g with considerable contribution of 3b. The lengthening of the transannular C-C bond (1.5579 Å) in connection with the overall bond geometry of the cyclopropane ring indicates a tendency towards an open form comparable to 1,6-methano[10]annulene 3g. In contrast to this finding in 2, the compounds 1 and 2 are methanol-modified with a tendency towards the formation of the cyclopropane ring.


Single crystal of the title compound were provided by Dr. Lorente of the Dpto. of Ch. Organique de the Univ. of Alcalá de Henares, Madrid.

The crystal structure has been solved by MULTAN11.1, Lessinger, Germain, Declercq and Woolfson (1978), and refined by weighted least-squares analysis up to the discrepancy indices of R and wR = 0.059, for 5449 observed reflections independent of which 4093 were considered observed with 0.2<2(0).

Crystal data are:
Formula, C₁₈H₁₃N₃S  Triclinic P I
b = 9.843 (2) Å  \( \mu = 17.17 \text{ cm}^{-1} \)
\( c = 10.545 (2) \) \( F(000) = 696 \)
\( a = 111.39 (1) \) \( \lambda = 1.5418 \)
\( \beta = 102.05 (1) \) \( \mu = 2.4 \)
\( \gamma = 83.77 (1) \) \( \mu = 2.4 \)
\( \delta = 696 \) \( \mu = 2.4 \)
\( n = 296.41 \)