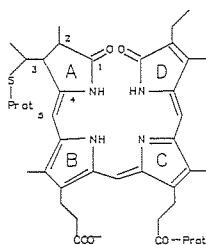


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-36 STRUCTURE AND FLEXIBILITY OF MODEL SYSTEMS FOR THE PLANT PIGMENT PHYTOCHROME.
By Christoph Kratky, Institut für physikalische Chemie, Universität Graz, A-8010 Graz, Austria.

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



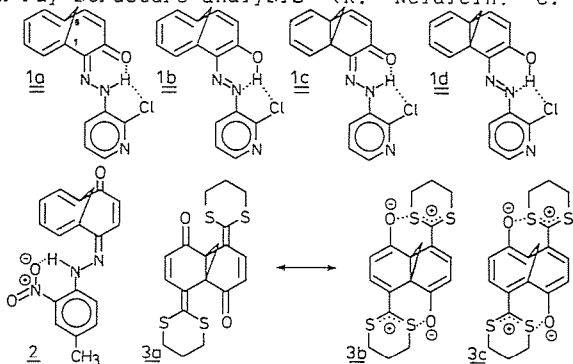
Crystal structures of several model systems for phytochrome were determined, including systems with the complete phytochrome chromophore and pairs of Z/E isomers (about the 4-5 bond) for an N-methylated dihydropyromethone and for a phytochrome analog with a carbonyl group in position 3. All structures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

The flexibility of the above molecules in the crystal is analyzed with a simple test based on Hirshfeld's "rigid bond" postulate (Hirshfeld, F.L. (1976). Acta Cryst. A32, 239-244) and its generalization to "rigid groups" (Rosenfield, R.E., Trueblood, K.N. & Dunitz, J.D. (1978). Acta Cryst. A34, 828-829), combined with a half-normal probability plot to assess the significance of non-zero Delta-values.

Radke, E. Hädicke, and A. Gieren, Chem. Ber. (1983) 116, 2881) revealed 2 to exist in a cycloheptatriene form and as the hydrazone 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 canonic structure of type 1c. Recently the cycloheptatriene form and the hydrazone tautomer (1a) 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 canonic structure 1c compared with the analogous form in the case of 2. Furthermore, the C-C-C angle of the CH₂ bridge is ca. 3° 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 paraquinoid) are associated with specific alternations of the bond lengths. Compared with 1 and 2, compound 3 has a naphthodiquinone-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 canonic formula 3a with considerable contribution of 3b. The lengthening of the transannular C-C bond (1.557 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 3c. In contrast to this finding in 3, the compounds 1 and 2 are methano[10]annulene systems with a tendency towards the formation of the cyclopropane ring.

09.2-37 COUPLING PRODUCTS OF DIAZONIUM SALTS WITH 3- AND 2-ALKOXY-1,6-METHANO[10]ANNULENES AND THE STRUCTURE OF AN ANALOGOUS 4,4a,8,8a-TETRAHYDRO-4a,8a-METHANO-1,5-NAPHTHOQUINONE.

By C.-P. Kaerlein, A. Gieren and H. Betz, Max-Planck-Institut f. Biochemie, Abt. Strukturforchung I, 8033 Martinsried, FRG. With respect to the 1,6-methano[10]annulene derivatives 1 and 2 valence tautomeric forms, the cycloheptatriene forms 1a, 1b and the norcaradiene forms 1c, 1d, as well as the tautomeric hydrazone forms (1a, 1c) in comparison to the azo forms (1b, 1d) have to be discussed. Compound 2 with respect to the molecular skeleton is a positional isomer of 1 with a para-arrangement of the semicyclic double bonds in contrast to an ortho one in 1. ¹H-NMR spectra indicated a norcaradiene form for 1 and a cycloheptatriene form for 2. Also for 3 a norcaradiene (3b) and a cycloheptatriene form (3c) have to be considered. An X-ray structure analysis (R. Neidlein, C.-M.



09.2-38 CRYSTAL STRUCTURE OF METHYL-N-(2,2-DICYANO-1-PHENYLETHENYL)THIOBENZIMIDATE

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

The crystal structure has been solved by MULTAN (Main, Hull, Lessinger, Germain, Declercq and Wolfson, 1978), and refined by weighted least-squares analysis up to the discrepancy indices of R and R_w = 0.057, for 5449 observed reflexions independent of which 4093 were considered observed with I < 2σ(I).

Crystal data are:

Formula, C₁₈H₁₃N₃S

Mr = 296.41

a = 18.853 (2) Å

b = 8.843 (2) "

c = 10.545 (2) "

α = 111.39 (1)°

β = 83.77 (1)°

γ = 102.05 (1)°

V = 1599.9 (6) Å³

Z = 4

μ = 17.17 cm⁻¹

F(000) = 696

λ = 1.5418

Triclinic P $\bar{1}$
D_x = 1.2306 g.cm⁻³

