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Chromotropisms of Imidazole Derivatives. III.[1,2] Crystal Structure of 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazole

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Synopsis. The molecular and crystal structure of the title compound was determined by the single-crystal X-ray analysis. The crystal is orthorhombic with a space group *Pbca*, a=15.161 (9), b=25.805 (5), c=9.948 (1) Å, and Z=8. The 4-nitrophenyl ring is nearly on a same plane with the imidazole ring, while the other two benzene rings make angles of 26.5° and 47.7°.

In the course of our study on the chromotropic behavior of the dimers of 2,4,5-triarylimidazolyl radicals obtained by the oxidation of 2,4,5-triaryl-1*H*-imidazole,[3] we have recently found that 4,5-bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-imidazole (**1**) crystallized in several colored states under different conditions. Crystallization of **1** from aqueous acetic acid gave an orange-yellow imidazolium acetate dihydrate (**I**), which exhibits sensitive color change from orange-yellow to red by drying, trituration, or heating.[1] The crystal structure of **I** showed that the solvents of crystallization played an essential role in crystal packing.[2] On the other hand, crystallization from dry benzene gave initially red needles (**II**), which changed their color and crystal form to light orange prisms (**III**) when the solution containing **II** had been allowed to stand for several days at room temperature. When exposed to AcOH–H_2O vapor, pulverized **III** changed to **I** after three days.

In order to clarify the relation between the color and the structure, a single-crystal X-ray analysis of **III** has been carried out.

Experimental

Data Collection. **III**; $C_{23}H_{19}N_3O_4$, F. W. 401.42, D_m=1.35 g cm^{-3} (aqueous KI), D_x=1.37 g cm^{-3}, μ (Mo$K\alpha$)=1.02 cm^{-1}. The unit-cell dimensions were refined on a Rigaku automated four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation (50 kV, 160 mA). The diffraction intensities were measured for a single crystal with approximate dimensions of 0.25×0.20×0.12 mm³ on the diffractometer by the ω—2θ scan technique at room temperature. The intensities of three standard reflections, measured after every 56 reflections, were stable within a 1% fluctuation. In the range of 2θ values up to 45°, 1252 independent structure factors ($|F_o|>3\sigma(F_o)$) were used for the structure determination. The intensities were corrected for Lorentz and polarization effects but not for absorption. All calculations were carried out on a FACOM M-380 computer at the Science Information Processing Center, University of Tsukuba.

Structure Dtermination. The structure was solved by the direct method (MULTAN 80).[4] All the 30 non-hydrogen atoms were found on the first E map calculated with 320$|E|$'s greater than 1.54. The atomic parameters were refined by the full-matrix least-squares method.[5] The atomic scattering factors, given by Cromer and Mann[6] for C, N, or O, and listed[7] on the table for H were used.

Refinement with isotropic temperature factors for C, N, O lowered the R factor to 0.216. One reflection 020 had $|F_o|$ abnormally lower than $|F_c|$. As it seemed to suffer the secondary extinction, the subsequent refinements were carried out without this reflection. Refinement with anisotropic temperature factors for non-hydrogen atoms reduced the R value to 0.093. All the hydrogen atoms were revealed on a difference Fourier map, which were included in the refinement with isotropic temperature factors. Finally the R value reduced to 0.037 (R_w=0.041). The residuals in the difference map were within in the range of +0.47—−0.22 e Å^{-3}. The atomic parameters[8] are listed in Table 1 (for the numbering diagram, see Fig. 1).

Results and Discussion

The selected bond distances and angles are shown in

Table 1. Atomic Coordinates of the Non-Hydrogen Atoms (×10⁴) and Equivalent Isotropic Temperature Factors with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
O(1)	5106(2)	112(1)	3463(3)	5.5	C(16)	3333(3)	3872(1)	4190(4)	3.7
O(2)	5112(2)	532(1)	1608(3)	7.7	C(17)	3117(3)	4344(1)	3617(4)	4.1
N(3)	4972(2)	502(1)	2805(3)	4.2	C(18)	2266(2)	4523(1)	3732(3)	3.5
C(4)	4649(2)	967(1)	3506(4)	3.2	C(19)	1649(3)	4245(1)	4446(3)	3.3
C(5)	4251(2)	915(1)	4744(4)	3.4	C(20)	1867(2)	3774(1)	5005(3)	3.0
C(6)	3930(2)	1356(1)	5361(3)	3.2	O(21)	1977(2)	4977(1)	3179(3)	5.1
C(7)	4016(2)	1841(1)	4753(3)	2.7	C(22)	2465(5)	5182(2)	2098(6)	6.6
C(8)	4459(2)	1877(1)	3537(4)	3.3	C(23)	2190(2)	2944(1)	7679(3)	2.8
C(9)	4766(2)	1438(1)	2894(4)	3.5	C(24)	2223(2)	3440(1)	8210(3)	3.4
C(10)	3582(2)	2290(1)	5338(3)	2.8	C(25)	1699(2)	3579(2)	9297(4)	3.8
N(11)	3151(2)	2306(1)	6504(3)	3.0	C(26)	1143(2)	3220(2)	9855(3)	4.1
C(12)	2752(2)	2789(1)	6545(3)	2.8	C(27)	1104(2)	2724(2)	9348(3)	4.2
C(13)	2960(2)	3068(1)	5406(3)	2.7	C(28)	1619(2)	2587(2)	8265(4)	3.7
N(14)	3494(2)	2745(1)	4664(3)	2.9	O(29)	598(2)	3322(1)	10929(3)	6.1
C(15)	2718(2)	3578(1)	4190(4)	2.7	C(30)	718(4)	3803(4)	11596(7)	8.8

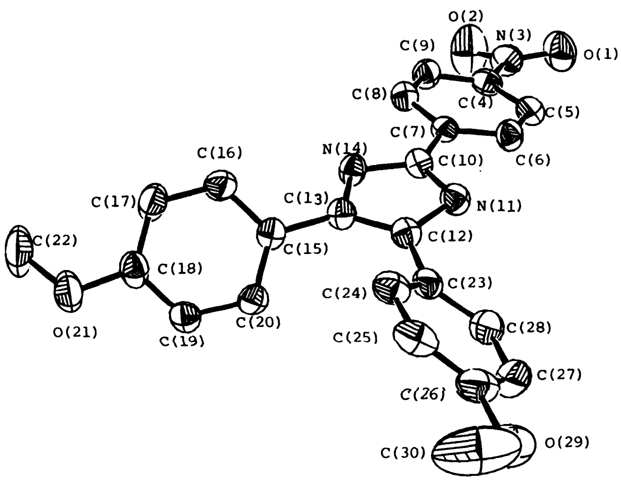

Fig. 1. A perspective view (ORTEP)[9] of the molecule with the atom numbering scheme. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability level.

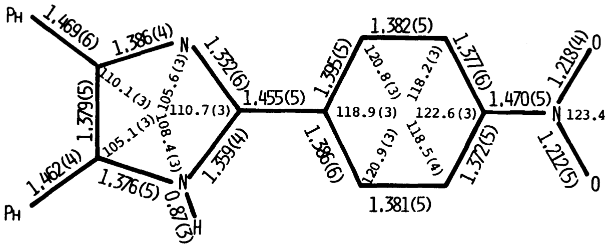

Fig. 2. Selected bond lengths and angles with estimated standard deviation in parentheses.

Fig. 2. Neither unusual bond distances nor angles in the molecule were observed. The molecular geometry of **III** is similar to that of **I**. The conformation of the molecule is illustrated in Fig. 1. The imidazole ring and the 4-nitrophenyl ring are nearly on a same plane. The dihedral angle [15.1°] between both rings is slightly larger than that [9.1°] in **I**. The other two benzene rings in **III** makes angles of 26.5° and 47.7° with the imidazole ring, while in **I** of 39.9° and 40.4°, respectively. This discrepancy is due to the presence of the solvents of crystallization in **I** and, by those, the benzene ring were forced to twist as to minimize the steric interaction between the ring and the water molecules.

Molecular packing of both compounds, on the other hand, are quite different with each other. The solvents of crystallization played an essential role in molecular packing in **I** and the molecules were packed in sheet parallel to the *ac* plane by the three-dimensional hydrogen-bonding network.[2] In **III**, as shown in Fig. 3, only a weak intermolecular hydrogen bonding was observed: N(11)(*x*,*y*,*z*)···H(14)-N(14)(*x*, 1/2−*y*,1/2+*z*) 3.190(5)Å and N(11)···1H(14) 2.46(3)Å, H(14)-N(14) 0.87(3)Å, and ϕ [N(11)-H(14)-N(14)] 141.8°. Other intermolecular atomic contacts are usual van der Waals distances and the shortest one is O(1)(*x*, *y*,*z*)···O(1) (1−*x*,−*y*,1−*z*) 3.129(5)Å.

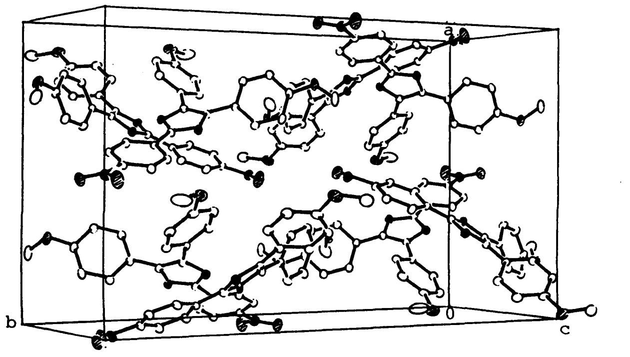

Fig. 3. The molecular packing diagram. ○: Carbon, ●: nitrogen, ⊘: oxygen.

As no significant π–π interaction between molecules was estimated from the crystal packing, the orange color of **III** is due to the absorption of the chromophore of **1** itself. This is consistent with the similarity of the longest UV maximum in solution (EtOH, 405 nm) to that in solid state (in Nujol, 410 nm).

References

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