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Crystal structure of N-isopropyl-1,8-naphthalimide $C_{15}H_{13}NO_2$

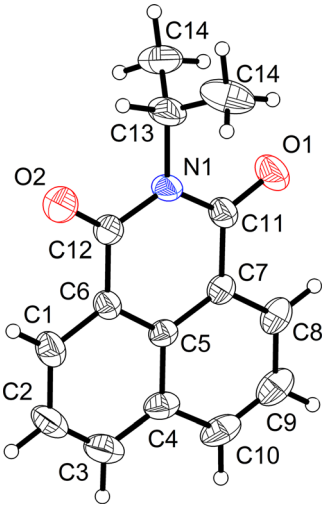

Figure: A view of the molecule. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as small spheres of arbitrary radii.

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Abstract

$C_{15}H_{13}NO_2$, orthorhombic, *Cmce* (no. 64), a = 7.0048(4) Å, b = 18.0939(7) Å, c = 19.2281(8) Å, V = 2437.0 Å^3, Z = 8, $R_{gt}(F)$ = 0.0614, $wR_{ref}(F^2)$ = 0.1989, T = 293.9(10) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.24 × 0.18 × 0.15 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	0.70 mm^{-1}
Diffractometer, scan mode:	Rigaku, ω scans
θ_{max}, completeness:	66.6°, 98 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3063, 1164, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 917
$N(param)_{refined}$:	107
Programs:	Rigaku[1], SHELX[2–4], Olex2[5]

1 Source of material

The title compound was synthesized according to the literature reported condensation methodology with slight modification.[6] According to the literature procedure, acetic acid and benzene were used as reaction solvent and eluent in column chromatography, respectively. The operating procedure is tedious and harmful to the environment. Therefore, we update the synthetic procedure with anhydrous ethanol, which is more removable than acetic acid. 1,8-naphthalic anhydride (1.98 g, 10 mmol) was mixed with 300 mL anhydrous ethanol. The mixture was heated to reflux for about 30 min. Then, isopropylamine (2 mL) was dissolved in 10 mL anhydrous ethanol and added dropwisely to the above reaction mixture. Subsequently, it was refluxed for another 2 h. The reaction progress was monitored by thin – layer chromatography (TLC). When the starting 1,8-naphthalic anhydride disappeared completely on the TLC, the refluxing apparatus was changed to distilling apparatus, removing 220 mL ethanol. The left mixture was cooled to 0 °C and stand still to precipitate crystalline. The precipitate was collected and washed throughly with ethanol. Analytical sample was obtained by double recrystallization in ethanol. The purified *N*-isopropyl-1,8-naphthalimide (100 mg) was dissolved in 10 mL ethanol in a 20 mL vial with parafilm covered. Three to five holes were made with the needle on the parafilm cover. After several days slow evaporation of the ethanol solution at room temperature, crystals generated at the bottom of the vial. Suitable crystal was selected for X-ray diffraction and data was collected.

2 Experimental details

The structure of *N*-isopropyl-1,8-naphthalimide was solved using ShelXt and refined by ShelXl through the Olex2 interface.[2,3] Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with *d*(C–H) = 0.93 Å, 0.96 Å, or 0.98 Å (–CH, $-CH_3$, $-CH_2$). U_{iso}(H) = 1.2U_{eq}(C) for CH or U_{iso}(H) = 1.5U_{eq}(C) for CH_3 and CH_2 groups.[2] C2/C3/C4/C8/C9/C10 were restricted by RIGU command to the reasonable thermal ellipsoids. According to the data refinement, the resolution was set to be 0.84 Å. The molecular graphics were drawn using the software DIAMOND with 50 % probability ellipsoids in the figure.[7]

3 Comment

The *N*-isopropyl-1,8-naphthalimide is a classical fluorescent dye with build-in naphthalimide framework, which has strong green fluorescence emission both in solution and in solid state when irradiated with 365 nm UV light. Therefore, various naphthalimide-containing fluorescent dyes were developed to be applied in chemsensor configuration, cell imaging, dye-sensitized solar cells device fabrication, etc.[8–12] Generally, the bromine atom is easy to be introduced to the four-position of naphthalic anhydride, generating 4-bromo-1,8-naphthalic anhydride. And the active bromine atom can be substituted by N/O based electron donating group, establishing the intramolecular electron push-pull effect with the electron withdrawing imide moiety. Together with the π system of naphthalene, the emission of naphthalimide-containing dye could be modified according to the requirement of material and/or optical devices. In case of ***N***-isopropyl-1,8-naphthalimide, those having 4-substituent naphthalimide derivatives can be configured as various longer wavelength emission dyes.[13–15] Chemsensors that can responsive to anions, cations, and/or small biological molecules were developed.

In the title crystal structure, the asymmetric unit contains half molecules. Both the bond lengths and the angles are in the expected ranges. Except for C14, the whole molecular framework is coplanar. The isopropyl was split into symmetrical geometry configuration and therefore C14 was distributed to both sides of the naphthalimide plane of symmetry. The bond lengths C11–O1 and C12–O2 are determined to be 1.212 and 1.218 Å, respectively, having the typical character of double bond. The C11/C12 of carbonly group is sp^2 hybridized. In addition, the bond length of C11–N1/C12–N1 (1.377 and 1.398 Å) is shorter than that of C13–N1 (1.494 Å) and has partial character of double bond. It indicates that the two carbonyl groups (C11–O1 and C12–O2) configured the imide group, having strong power of electron-withdrawing. Totally, the π system of naphthalene and the electron acceptor (imide group) jointly configured the intramolecular electron "push-pull" effect in a fluorescent dye molecular system. Once more stronger electron donating unit was introduced furtherly, various modificable fluorescent naphthalimide-containing dyes can be widely developed.[16–19] The adjacent parallel molecules are jointed by strong $\pi\cdots\pi$ interaction. The distance between the naphthalimide plane (C1/C2/C4/C5/C6/C7/C8/C9/C10//C11/C12/N1^{i1}, *i*1:*x*, *y*, *z*) and the parallel one (C1/C2/C4/C5/C6/C7/C8/C9/C10//C11/C12/N1^{i2} *i*2:1/2–*x*, +*y*, 3/2–*z*) is determined to be 3.502 Å and the parallel shift is 1.205 Å, corresponding to the parallel-displaced geometry.[20] Additionally, typical intramolecular C–H···O interactions are established. The configuration of isopropyl was locked by the C14–H14A···O1^{i1}, which makes the plane of C14/C13/C14^{i3} (*i*3: 1–*x*, +*y*, +*z*) perpendicular to the plane of the naphthalimide plane (C1/C2/C4/C5/C6/C7/C8/C9/C10//C11/C12/N1^{i1}). The distance of C14···O1 and H14A···O1 is estimated to be 2.975 and 2.430 Å with the C–H···O angle being 115.7°. Of course, another carbonyl O2 also involved in the intermolecular hydrogen bond construction. The H···O contact is C14^{i4}–H14C···O2 (*i*4: 1/2+*x*, 1/2–*y*, 1–*z*) with the H···O distance being 2.706 Å. Both the inter- and intra-molecular C–H···O angles are in agreement with the above mentioned survey.[21,22] The construction of weak hydrogen bonds in the crystal is significant to understand the emission properties of the fluorescent dyes in solid state.[23–27] Therefore, reasonable introduction of different inter- and/or intra-molecular hydrogen bonds into the crystal lattice is key to modify the ratio between the radiative and nonradiative channels.[28,29] Once the stronger intramolecular interactions are established between dye molecules, more nonradiative channels will be established for the excited molecules and thus quenching the fluorescent emission.[30–33]

In the crystal, the dye molecules are regularly packed by the intermolecular force, including hydrogen bonds and $\pi\cdots\pi$ interactions. The driving force for the title molecule packing parallel to each other along the axis ***a*** is based on the $\pi\cdots\pi$ interaction. While, the parallel molecules are joined by the hydrogen bonds.[34,35] The weaker interactions distributed in the titly packed dye molecules turn on/off the highly emissive character in crystal/solid state.[34–36] With the establishing of the T-shaped $\pi\cdots\pi$ interaction, the naphthimide part promotes the tightly packed model. However, the perpendicular isopropyl inhibited this packing trend in some degree. The comprehensive result leads to an appropriate emission channel and highly green emission character of naphthalimide.[37–41] The nonradiative channel of

excited dye molecules is easy to be interfered by the external environment. Therefore, it is very important to intra- and inter-molecular interactions, establishing a higher proportion emission channel.[42,43] To the title *N*-isopropyl-1,8-naphthalimide, the unique packing model, together with its intramolecular electron "push-pull" system, does establish its recognizable optical property and biological application.[44,45] It also shows that the reasonable introduction of heteroatom-containing moiety and/or aromatic ring system is an effective way in fluorescent dye designing.[46–48] In conclusion, the title molecules are staggered layer by layer along with axis ***b*** and ***c*** by the strong $\pi\cdots\pi$ interaction. While, the hydrogen bonds based on H···O contacts joint the parallel adjacent molecules.

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