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Trimellitimide ($C_9H_5NO_4$) and *N*-Ethyltrimellitimide ($C_{11}H_9NO_4$)

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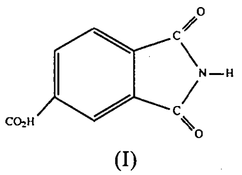
Abstract

(I) 1,3-Dihydro-1,3-dioxoisoindole-5-carboxylic acid (trimellitimide) and (II) 2-ethyl-1,3-dihydro-1,3-dioxoisoindole-5-carboxylic acid (*N*-ethyltrimellitimide) each have one molecule in the asymmetric unit. The hydrogen bonding in both instances produces carboxylic acid dimers. In (I), additional hydrogen bonding through the 'phthalimido' groups links the acid dimers into infinite chains.

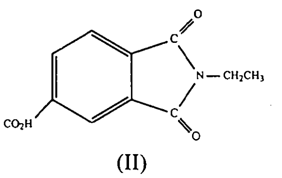
Comment

As part of a general study of the stability of organic peracids and peracid salts (Kariuki & Jones, 1992), and in particular of the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the structures of trimellitimide and *N*-ethyltrimellitimide.

The bond angles and distances observed for both structures are similar to those reported for phthalimide (Matzat, 1972), *N*-(4-bromophenyl)phthalimide (Ribar, Stankovic & Halasi, 1976) and *N*-(4-iodophenyl)phthalimide (Ribar, Stankovic, Herak, Halasi & Djuric, 1974). Long C=O and short C=O bonds have been measured for the structures of (I) and (II), suggesting a disordered model for the carboxyl groups, commonly observed in *p*-substituted benzoic acids (Leiserowitz, 1976).



(I)



(II)

Molecules of (I) and (II) have similar geometries. The phthalimido groups (excluding H atoms) *A*(I) and *A*(II) are planar to within 0.027 and 0.032 Å, respectively. The carboxyl groups [O(90)C(9)O(91)] make angles to these planes of 6.5 and 6.7°, respectively. For molecule (II), the C(8)—N(1)—C(10)—C(11) torsion angle is 82.1°.

Fig. 2 is a *PLUTO* (Motherwell & Clegg, 1978) plot of the structure of (I) illustrating the intermolecular hydrogen-bonding pattern. The carboxylic acid groups are hydrogen bonded to form the familiar dimer motif [O···O=C 2.626 (5) Å]. In addition, the phthalimido ends of the dimers are hydrogen bonded [N—H···O=C 1.832 (5), N···O=C 2.980 (5) Å], linking dimers related by a [101] translation into infinite chains. These chains are stacked along the *b* axis and held together by π–π interactions between phthalimido groups.

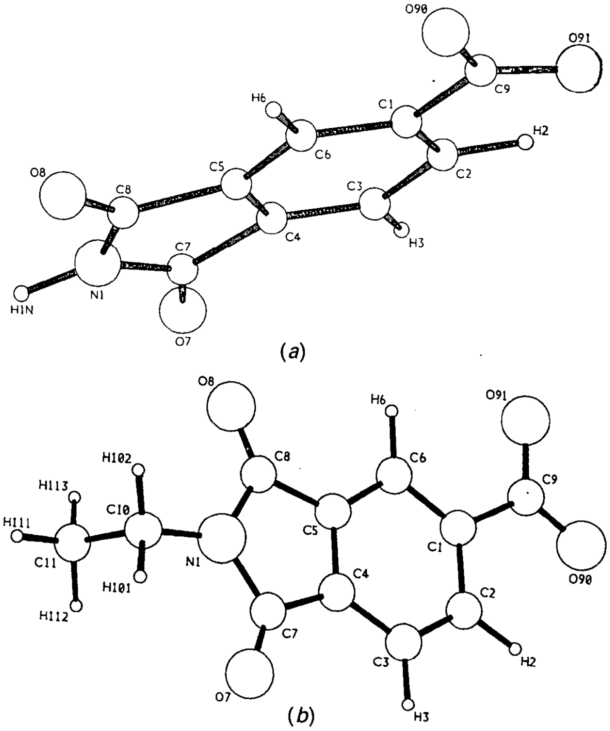


Fig. 1. Atom-numbering scheme for (*a*) (I) and (*b*) (II).

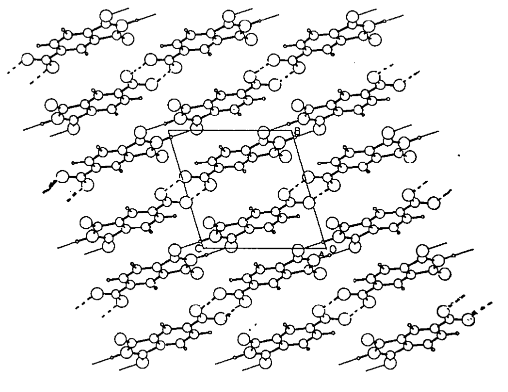


Fig. 2. Packing diagram for (I), viewed down the *a* axis, demonstrating the generation of infinite chains through hydrogen bonding.

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Fig. 3(*a*) shows the packing arrangement of molecules of (II). Hydrogen bonded (carboxylic acid) dimers are again formed [O···O=C 2.610 (3) Å]. The *N*-alkyl substituent, however, now makes further hydrogen bonding impossible. The dimers held together by weak van der Waals forces are stacked along the *a* axis forming a ribbon-type structure. The ribbons are stacked along the *c* axis connected by short C—H···O contacts (shown in Fig. 3*b*) and π–π interactions between phthalimido groups. Hence 'blocks' of molecules are formed, stacked along the *b* axis and held together by van der Waals forces. This is an almost identical arrangement to that seen for one polymorphic form of the *p*-amidobenzoic acid (Feeder & Jones, 1993). In that particular case there was evidence that the structure could be adopted by compounds with various lengths of the (straight) alkyl chain. Powder X-ray analysis of the trimellitimide series has suggested that a similar situation arises, although no other crystals suitable for full structural study have been obtained. The profile of the simulated pattern of (II) and of the measured patterns for the *n*-butyl and *n*-pentyl derivatives are similar. An estimate of the *b*-axis dimension may be obtained from the location of the (020) reflection 2θ position in the measured powder patterns and a plot of this value *versus* the number of C atoms in the alkyl chain is linear [as also seen for *p*-amidobenzoic acids (Feeder & Jones, 1993)].

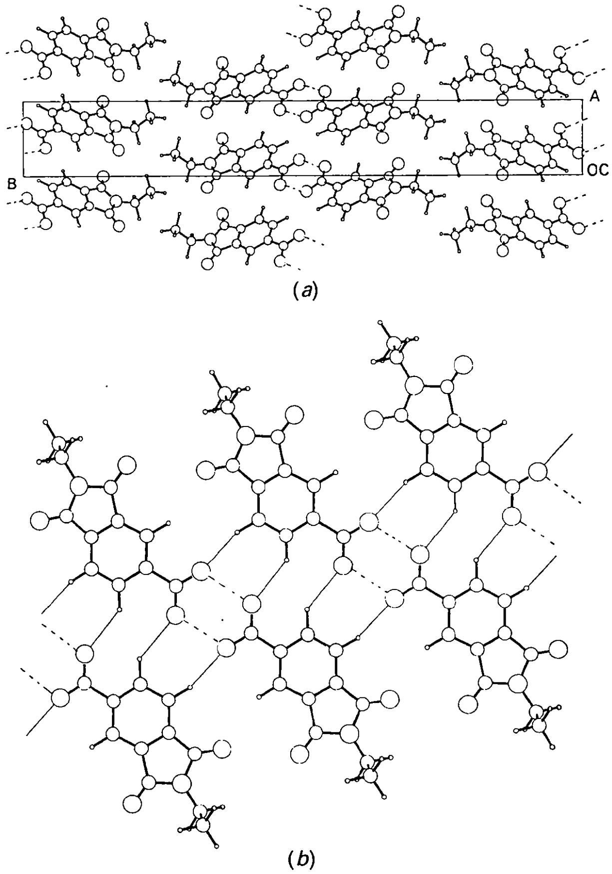

Fig. 3(*a*). Packing arrangment of the dimers resulting from hydrogen bonding in (II) as viewed down the *c* axis. (*b*) The side-by-side arrangement of dimers in (II) (viewed perpendicular to the benzene ring). Also shown are some short intermolecular CH···O contacts.

Experimental

Compound (I)

Crystal data

$C_9H_5NO_4$
$M_r = 191.15$
Triclinic
$P\bar{1}$
$a = 6.537$ (4) Å
$b = 8.161$ (3) Å
$c = 8.450$ (6) Å
$\alpha = 70.44$ (2)°
$\beta = 73.90$ (2)°
$\gamma = 76.42$ (3)°
$V = 403$ Å^3
$Z = 2$

$D_x = 1.574$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.12$ mm^{-1}
$T = 295$ K
Cuboid
0.1 × 0.1 × 0.1 mm
White, transparent

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2107 measured reflections
1940 independent reflections
1083 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 28$°
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.057$
$wR = 0.057$
$S = 1.21$
1083 reflections
129 parameters
Unit weights applied
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.40$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_{11}H_9NO_4$
$M_r = 219.20$
Monoclinic
$P2_1/n$
$a = 5.078$ (1) Å
$b = 37.909$ (7) Å
$c = 5.184$ (1) Å
$\beta = 95.59$ (2)°
$V = 993$ Å^3
$Z = 4$
$D_x = 1.46$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–15°
$\mu = 0.11$ mm^{-1}
$T = 295$ K
Plate-like
0.3 × 0.2 × 0.1 mm
White, transparent

Data collection

Enraf-Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3234 measured reflections
2890 independent reflections
1102 observed reflections [$F > 6\sigma(F)$]
$R_{\text{int}} = 0.215$
$\theta_{\text{max}} = 30°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 53$
$l = 0 \rightarrow 7$
2 standard reflections frequency: 60 min intensity variation: none

Refinement

Refinement on F
$R = 0.099$
$wR = 0.099$
$S = 1.19$
1102 reflections
152 parameters
Unit weights applied
$(\Delta/\sigma)_{\text{max}} = 0.256$
$\Delta\rho_{\text{max}} = 0.60$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.51$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(I)				
N(1)	−0.2752 (5)	0.1016 (5)	0.8728 (4)	0.039
O(7)	−0.5096 (4)	0.0167 (4)	0.7674 (3)	0.048
O(8)	0.0048 (5)	0.2167 (5)	0.8906 (4)	0.059
O(90)	0.4093 (5)	0.4601 (4)	0.2126 (3)	0.049
O(91)	0.2815 (5)	0.3917 (4)	0.0273 (3)	0.051
C(1)	0.1039 (6)	0.3155 (5)	0.3211 (4)	0.020
C(2)	−0.0558 (6)	0.2589 (5)	0.2822 (5)	0.037
C(3)	−0.2182 (6)	0.1824 (5)	0.4133 (5)	0.037
C(4)	−0.2122 (6)	0.1652 (5)	0.5789 (4)	0.032
C(5)	−0.0530 (6)	0.2237 (5)	0.6162 (4)	0.034
C(6)	0.1103 (6)	0.2993 (5)	0.4890 (5)	0.035
C(7)	−0.3559 (6)	0.0852 (5)	0.7460 (5)	0.034
C(8)	−0.0931 (6)	0.1843 (5)	0.8060 (5)	0.037
C(9)	0.2790 (6)	0.3953 (5)	0.1790 (5)	0.034
(II)				
N(1)	0.3327 (22)	0.1654 (2)	0.3952 (20)	0.052
O(7)	0.0027 (20)	0.1431 (2)	0.6191 (18)	0.070
O(8)	0.6552 (20)	0.1710 (2)	0.1094 (20)	0.070
O(90)	0.2876 (18)	0.0063 (2)	−0.2769 (17)	0.059
O(91)	0.6206 (17)	0.0402 (2)	−0.3719 (17)	0.055
C(1)	0.3464 (22)	0.0619 (3)	−0.0603 (20)	0.036
C(2)	0.1469 (23)	0.0532 (3)	0.0968 (22)	0.048
C(3)	0.0727 (25)	0.0774 (3)	0.2745 (23)	0.048
C(4)	0.1952 (24)	0.1105 (3)	0.2891 (22)	0.041
C(5)	0.3925 (24)	0.1182 (3)	0.1356 (22)	0.041
C(6)	0.4842 (23)	0.0940 (3)	−0.0411 (22)	0.041
C(7)	0.1536 (26)	0.1396 (3)	0.4571 (24)	0.045
C(8)	0.4909 (26)	0.1540 (3)	0.1992 (24)	0.048
C(9)	0.4222 (24)	0.0344 (3)	−0.2480 (23)	0.040
C(10)	0.3540 (32)	0.1998 (3)	0.5155 (29)	0.066
C(11)	0.2047 (38)	0.2276 (4)	0.3553 (33)	0.088

Table 2. *Selected geometric parameters* (Å, °)

	(I)	(II)
C(1)—C(2)	1.389 (5)	1.399 (15)
C(2)—C(3)	1.393 (5)	1.378 (16)
C(3)—C(4)	1.369 (5)	1.398 (16)
C(4)—C(5)	1.388 (5)	1.370 (16)
C(5)—C(6)	1.380 (5)	1.406 (15)
C(6)—C(1)	1.392 (5)	1.403 (15)
C(7)—C(4)	1.496 (5)	1.435 (15)
C(7)—N(1)	1.373 (7)	1.394 (15)
C(7)—O(7)	1.204 (4)	1.198 (14)
C(8)—C(5)	1.485 (5)	1.473 (16)
C(8)—N(1)	1.393 (5)	1.423 (15)
C(8)—O(8)	1.204 (5)	1.185 (15)
C(9)—C(1)	1.497 (5)	1.503 (15)
C(9)—O(90)	1.237 (5)	1.264 (13)
C(9)—O(91)	1.288 (5)	1.266 (16)
N(1)—C(10)	-	1.444 (14)
C(10)—C(11)	-	1.500 (20)
C(6)—C(1)—C(2)	122.6 (4)	123.2 (11)
C(9)—C(1)—C(2)	119.6 (3)	117.3 (11)
C(9)—C(1)—C(6)	117.8 (3)	119.4 (11)
C(3)—C(2)—C(1)	120.3 (4)	119.5 (12)
C(4)—C(3)—C(2)	117.5 (3)	118.9 (12)
C(7)—C(4)—C(5)	107.5 (3)	110.4 (12)
C(3)—C(4)—C(5)	121.8 (3)	120.4 (11)
C(3)—C(4)—C(7)	130.6 (3)	129.2 (12)
C(6)—C(5)—C(4)	121.9 (3)	123.2 (12)
C(8)—C(5)—C(4)	107.9 (3)	108.5 (11)
C(8)—C(5)—C(6)	130.1 (4)	128.3 (12)
C(5)—C(6)—C(1)	116.0 (3)	114.6 (12)
N(1)—C(7)—C(4)	106.3 (3)	105.2 (11)
N(1)—C(7)—O(7)	126.2 (3)	124.0 (12)
O(7)—C(7)—C(4)	127.5 (5)	130.7 (13)
N(1)—C(8)—C(5)	106.0 (3)	103.8 (12)
N(1)—C(8)—O(8)	124.9 (3)	125.6 (13)
O(8)—C(8)—C(5)	129.0 (4)	130.5 (13)
O(91)—C(9)—O(90)	124.4 (3)	122.4 (12)
O(90)—C(9)—C(1)	119.3 (3)	119.4 (12)
O(91)—C(9)—C(1)	116.2 (3)	118.2 (11)
C(11)—C(10)—N(1)	-	112.4 (13)
C(7)—N(1)—C(8)	112.2 (3)	112.1 (11)
C(10)—N(1)—C(8)	-	124.1 (13)
C(10)—N(1)—C(7)	-	123.8 (12)

Standard reflections were recentred every 100 reflections and scanned every hour to check for crystal movement and stability. The stuctures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares analysis using *SHELX*76 (Sheldrick, 1976). The ring, alkyl and, in the case of (I), amino H atoms were fixed geometrically and refined with isotropic displacement parameters. The carboxylic H-atom coordinates could not be located from the difference Fourier map for either structure. All non-H atoms were refined with anisotropic displacement parameters. The relatively high R value for (II) is believed to be a result of the poor quality of the crystal. The crystals were very plate-like and frequently consisted of several individual platelets fused together.

We acknowledge support from the SERC (studentship for NF). We are grateful to Solvay Interox PLC (and in particular Dr A. James) for the provision of samples and numerous discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71777 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1019]

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t-3-Isopropyl-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one, $C_{20}H_{24}N_2O$

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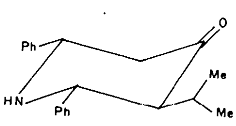
Abstract

The diazepine ring adopts a slightly distorted chair conformation. The phenyl substituents adopt equatorial orientations. The unsymmetrical distortion arises from the torsional strains between the phenyl and isopropyl groups. The compound exists as a dimer exhibiting intermolecular N—H···O hydrogen bonding.

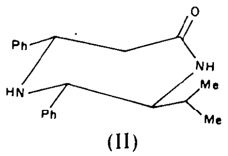
Comment

A wide range of diazepines have been identified as potential drugs for various diseases (Hamor & Martin, 1984). Most of them contain benzene rings fused to the diazepine ring at the 2,3 and/or 6,7 position. The fusion of the aromatic hydrocarbons makes the boat form of the diazepines more stable. We have been interested in the conformational effect of substituting (rather than fusing) the phenyl rings to the 2 and 7 positions of the diazepine ring.

The Beckmann rearrangement of the oxime derivative of the 3-isopropylpiperidone (I) has been reported to afford the diazepine (II) exclusively, though there are two possibilities for the ring opening to afford two isomers, *viz.* the 3-isopropyldiazepinone (II) and a 6-isopropyldiazepinone (Baliah, Lakshmanan & Pandiarajan, 1978). Schmidt reaction of the piperidone (I) has also been reported (Mohan, 1985) to yield the diazepine (II). Though the determination of the regiochemistry of migration may appear to be trivial, the formation of an abnormal product in the Schmidt rearrangement of the related ketone, namely 2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one, justifies the need for the confirmation of the regiochemistry. Instead of migration of the α bond alone, both α and β bonds were found to migrate (Senthilkumar & Jeyaraman, 1993). We were interested in determining whether there has been any configurational change during the Schmidt rearrangement. For this purpose, *t*-3-isopropyl-*r*-2,-*c*-6-diphenylpiperidone (I) was prepared and converted to its hydrochloride. The hydrochloride (5.11 g, 15.53 mmol) was dissolved in concentrated H_2SO_4 (25 ml) and one equivalent of sodium azide (1.24 g, 19.07 mmol) was added in small portions for a period of 1 h. After the addition was over, the solution was stirred for another hour and poured slowly onto crushed ice and basified (pH 8) with cold concentrated NaOH solution. The precipitated solid was separated by filtration through a Buchner funnel, washed several times to remove excess sodium hydroxide and dried. Recrystallization from benzene followed by ethanol afforded colourless crystals of *t*-3-isopropyl-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (II); m.p. 461–462 K [literature value 461 K (Baliah, Lakshmanan & Pandiarajan, 1978)].



(I)



(II)

Both the phenyl groups of the title compound are *trans* to the isopropyl group as in the parent piperidone (I). This observation indicates that the relative geometry of the substituents is preserved during the Schmidt reaction, thus confirming it to be an intramolecular rearrangement.

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