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N,*N*′-Bis(2-carboxyethyl)-1,4,5,8-naphthalenetetracarboxylic diimine dimethylformamide disolvate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.108
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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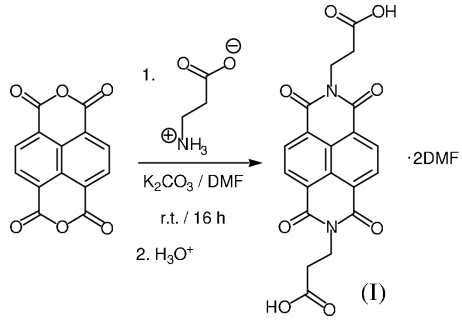
In the title compound, $C_{20}H_{14}N_2O_8\cdot 2C_3H_7NO$, the essentially planar $C_{20}H_{14}N_2O_8$ molecule is centrosymmetric and is hydrogen bonded *via* the carboxylic acid H atoms to the aldehyde O atom of the dimethylformamide molecules.

Comment

The redox-active nature of naphthalene diimides, when combined with their intercalating properties (Vicic *et al.*, 2000; Guelev *et al.*, 2002), make them a useful electron acceptor for studies involving electron transport in nucleic acid-based constructs. One construct that shows potential in this regard involves a peptide backbone made of repeating 2-aminoethylglycine units (Eriksson *et al.*, 1996). Hence, naphthalene diimides that possess either carboxylic acid or amine functional groups tethered through the diimide N atom may become useful synthons with which to append peptide nucleic acid strands. We report here the novel synthesis and X-ray structure of the title compound, (I), containing β-alanyl side chains.



The synthesis of (I) was achieved by condensing commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride with β-alanine in the presence of K_2CO_3 at room temperature overnight. This method is extremely mild compared with the standard preparation methods [dimethylformamide (DMF), 383–393 K] and can find use for heat-sensitive or volatile amines. The added K_2CO_3 acts as both a base and a dehydrating agent, driving the associated equilibria to completion. The low solubility of the dicarboxylate salt in DMF, and the high solubility in water, allow the easy separation and purification of (I) by filtration and acidification.

The centrosymmetric molecular structure of (I) is shown in Fig. 1. Clearly indicated are the two DMF solvent molecules of crystallization, which are connected through a hydrogen-bonding interaction between the acidic H atom, H14, and DMF atom O16 (Table 1).

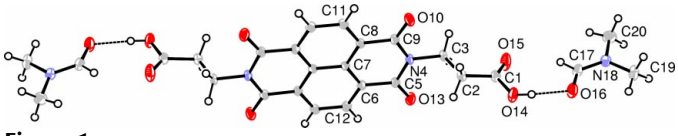


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level.

In the crystal structure there is very little interaction between neighbouring diimides, despite the essentially planar 20-atom core. This result is consistent with our recent report on a [2]catenane, in which the naphthalene diimide units also failed to π-stack (Fallon *et al.*, 2004).

Experimental

β-Alanine (1.28 g, 14.3 mmol) and K_2CO_3 (1.76 g, 12.8 mmol) were added to a stirred solution of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.55 g, 5.78 mmol) in dry DMF (40 ml). The reaction mixture was stirred overnight and then filtered. The collected precipitate was dissolved in water (20 ml) and concentrated HCl_{aq} was added until the pH of the solution was less than 3. The resulting precipitate was collected at a pump, washed with water and dried to yield (I) (2.30 g, 97%) as a pink solid. Vapour diffusion of H_2O into a DMF solution of (I) afforded single crystals suitable for X-ray analysis. ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.87 (*s*, 4H, Ar-H), 3.51 (*t*, J = 7.7 Hz, 4H, CH_2), 1.87 (*t*, J = 7.7 Hz, 4H, CH_2); ^{13}C NMR (75 MHz, d_6-DMSO): δ 173.2, 163.3, 131.2, 127.2, 126.9, 36.9, 32.9; ESI: m/z 410.0 ($[M]^-$).

Crystal data

$C_{20}H_{14}N_2O_8{\cdot}2C_3H_7NO$
M_r = 556.52
Triclinic, $P\overline{1}$
a = 4.9519 (1) Å
b = 10.8758 (2) Å
c = 12.9078 (3) Å
α = 111.985 (1)°
β = 95.578 (1)°
γ = 94.095 (1)°
V = 637.17 (2) Å^3
Z = 1
D_x = 1.450 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11976 reflections
θ = 3.1–28.3°
μ = 0.11 mm^{-1}
T = 123 (2) K
Plate, red
0.26 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
11 976 measured reflections
3132 independent reflections
2266 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 28.3°
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.108
S = 1.06
3132 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.1167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O14—H14···O16	0.84	1.80	2.6315 (14)	173

All H atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 0.99 Å and an O—H distance of 0.84 Å, and were included in the refinement in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(carrier atom) (1.5U_{eq} for methyl and hydroxy H atoms).

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Eriksson, M. & Nielsen, P. E. (1996). *Nat. Struct. Biol.* **3**, 410–413.
Fallon, G. D., Lee, M. A.-P., Langford, S. J. & Nichols, P. J. (2004). *Org. Lett.* **6**, 655–658.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Guelev, V., Sorey, S., Hoffman, D. W. & Iverson Brent, B. L. (2002). *J. Am. Chem. Soc.* **124**, 2864–2865.
Nonius (1997–2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Vicic, D. A., Odom, D. T., Nunez, M. E., Gianolio, L. W., McLaughlin, L. W. & Barton, J. K. (2000). *J. Am. Chem. Soc.* **122**, 8603–8611.