Z. Kristallogr. NCS 214 (1999) 187–188

Crystal structure of bis[*R*-(+)-1-(1-naphthyl)ethylammonium]squarate, $[C_{12}H_{14}N]_2C_4O_4$

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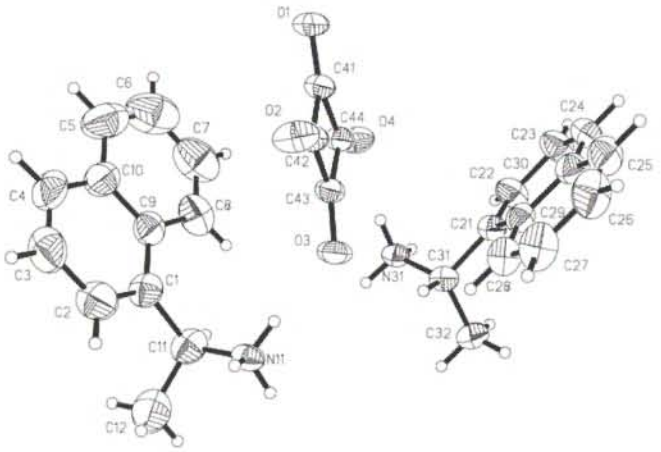
Received October 7, 1998, CCDC-No. 1267/21



Abstract

$C_{28}H_{28}N_2O_4$, monoclinic, $P12_11$ (No. 4), a = 12.373(2) Å, b = 7.367(2) Å, c = 14.100(3) Å, β = 109.26(2)°, V = 1213.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.039, $R_w(F^2)$ = 0.105, T = 291 K.

Source of material

The compound was prepared bys slowly adding an ethanolic solution of *R*-(+)-1-(1-naphthyl)ethylamine free base to a water solution of squaric acid with continuous stirring by room temperature for 30 minutes in 2:1 molecular ratio. The product was purrified by recrystallization water-ethanol mixture (1:1). After addition of amine the mixture was stirred at ambient temperature for 30 minutes. Colorless crystals were grown by slow evaporation from aqueous solution at room temperature.

Discussion

The structure determination was undertaken in order to choose special molecules and crystal growth methods which are of major importance for obtaining single crystals of large size and good quality for nonlinear optical applications. One main advantage of the organic materials is the possibility to optimize the nonlinearity by varying the molecular structure. Noncentrosymmetry of the crystal structure is a basic requirement for nonlinear optical behaviour [1]. In this paper is described an acentric crystal structure with potential nonlinear application.

The two *R*-(+)-1-(1-naphthyl)ethylamine molecules adopt the two protons from the the squaric acid. The squarate dianion C_4O_4 is a cyclic compound with the symmetry likely to be D_{4h}. In the crystal, anions and cations are linked via hydrogen bonds and a three-dimentional network is formed.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.50 x 0.50 x 0.55 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.84 cm^{-1}
Diffractometer, scan mode:	Nonius Mach3, ω/2θ
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5797, 5549
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5010
$N(param)_{refined}$:	312
Programs:	SHELXS-90 [2], SHELXL-93 [3], SHELXTL-Plus [4], PARST95 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11A)	2a	0.0405	0.4233	0.3964	0.057
H(11B)	2a	0.0301	0.6102	0.4254	0.057
H(11C)	2a	0.0530	0.4665	0.5001	0.057
H(31A)	2a	−0.0067	0.3418	0.0888	0.051
H(31B)	2a	0.0073	0.5319	0.1178	0.051
H(31C)	2a	−0.0402	0.4825	0.0124	0.051
H(2)	2a	0.2538	0.3869	0.6480	0.096
H(3)	2a	0.3719	0.1447	0.7194	0.117
H(4)	2a	0.4529	−0.0248	0.6256	0.111
H(5)	2a	0.4690	−0.1035	0.4596	0.133
H(6)	2a	0.4199	−0.0501	0.2912	0.158
H(7)	2a	0.2964	0.1833	0.2171	0.135
H(8)	2a	0.2244	0.3686	0.3107	0.096
H(11)	2a	0.2045	0.5635	0.4048	0.077
H(12A)	2a	0.1970	0.8015	0.5057	0.141
H(12B)	2a	0.3109	0.6994	0.5632	0.141
H(12C)	2a	0.2025	0.6734	0.5960	0.141
H(22)	2a	−0.1749	0.3349	−0.0983	0.072
H(23)	2a	−0.2848	0.1062	−0.1974	0.084
H(24)	2a	−0.4071	−0.0595	−0.1406	0.080
H(25)	2a	−0.4919	−0.1270	−0.0105	0.089
H(26)	2a	−0.5109	−0.0683	0.1413	0.101
H(27)	2a	−0.4001	0.1562	0.2443	0.094
H(28)	2a	−0.2688	0.3170	0.1960	0.074
H(31)	2a	−0.1475	0.4349	0.1526	0.054
H(32A)	2a	−0.1619	0.7308	0.0932	0.089
H(32B)	2a	−0.2835	0.6410	0.0557	0.089
H(32C)	2a	−0.2133	0.6624	−0.0180	0.089

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*a*	0.0718(1)	−0.3064(1)	0.22360(8)	0.0617(6)	0.0256(4)	0.0440(5)	0.0045(4)	0.0200(5)	−0.0045(4)
O(2)	2*a*	−0.0142(1)	−0.1411(2)	0.39492(8)	0.0885(8)	0.0385(6)	0.0464(6)	0.0140(6)	0.0409(6)	0.0088(5)
O(3)	2*a*	−0.0309(1)	0.2594(1)	0.29486(8)	0.0654(7)	0.0282(5)	0.0416(5)	0.0081(5)	0.0120(5)	−0.0081(4)
O(4)	2*a*	0.0380(1)	0.0906(1)	0.11305(8)	0.0664(7)	0.0330(5)	0.0389(5)	0.0092(5)	0.0265(5)	0.0058(4)
C(41)	2*a*	0.0406(1)	−0.1521(2)	0.23980(9)	0.0435(7)	0.0263(6)	0.0310(6)	−0.0004(5)	0.0136(5)	−0.0030(5)
C(42)	2*a*	0.0033(1)	−0.0750(2)	0.3194(1)	0.0480(7)	0.0281(6)	0.0326(6)	0.0033(5)	0.0154(5)	−0.0012(5)
C(43)	2*a*	−0.0057(1)	0.1043(2)	0.2737(1)	0.0425(6)	0.0276(6)	0.0302(6)	0.0022(5)	0.0094(5)	−0.0033(5)
C(44)	2*a*	0.0270(1)	0.0267(2)	0.19181(9)	0.0421(6)	0.0260(6)	0.0320(6)	0.0007(5)	0.0118(5)	−0.0019(5)
N(11)	2*a*	0.0662(1)	0.5052(2)	0.44510(9)	0.0536(6)	0.0272(5)	0.0345(5)	−0.0012(5)	0.0166(5)	−0.0014(4)
N(31)	2*a*	−0.03653(9)	0.4524(1)	0.07450(8)	0.0419(5)	0.0250(5)	0.0363(5)	−0.0009(4)	0.0145(4)	−0.0004(4)
C(1)	2*a*	0.2581(1)	0.3593(2)	0.5084(1)	0.0521(8)	0.0413(8)	0.0506(8)	−0.0002(6)	0.0164(7)	0.0093(7)
C(2)	2*a*	0.2844(2)	0.3169(3)	0.6082(1)	0.088(1)	0.051(1)	0.053(1)	0.0001(9)	0.0212(9)	0.0072(8)
C(3)	2*a*	0.3561(2)	0.1710(3)	0.6516(2)	0.099(2)	0.058(1)	0.056(1)	−0.007(1)	−0.002(1)	0.0166(9)
C(4)	2*a*	0.4023(2)	0.0681(3)	0.5954(2)	0.066(1)	0.043(1)	0.090(2)	0.0016(8)	−0.005(1)	0.014(1)
C(5)	2*a*	0.4193(2)	−0.0089(3)	0.4307(3)	0.066(1)	0.061(1)	0.145(3)	0.004(1)	0.041(1)	−0.013(2)
C(6)	2*a*	0.3901(3)	0.0231(5)	0.3304(3)	0.105(2)	0.100(2)	0.136(3)	−0.013(2)	0.075(2)	−0.036(2)
C(7)	2*a*	0.3163(3)	0.1640(5)	0.2859(2)	0.095(2)	0.107(2)	0.081(2)	−0.025(2)	0.047(1)	−0.024(2)
C(8)	2*a*	0.2729(2)	0.2739(3)	0.3417(1)	0.059(1)	0.080(1)	0.055(1)	−0.015(1)	0.0215(8)	−0.0043(9)
C(9)	2*a*	0.3005(1)	0.2464(2)	0.4470(1)	0.0399(7)	0.0471(9)	0.0563(9)	−0.0076(6)	0.0124(6)	−0.0015(7)
C(10)	2*a*	0.3746(2)	0.1002(3)	0.4917(2)	0.0437(8)	0.0438(9)	0.087(1)	−0.0044(7)	0.0114(8)	−0.0026(9)
C(11)	2*a*	0.1913(2)	0.5314(2)	0.4675(1)	0.0539(8)	0.0393(8)	0.063(1)	−0.0002(7)	0.0223(8)	0.0142(7)
C(12)	2*a*	0.2289(2)	0.6912(3)	0.5398(2)	0.074(1)	0.0377(9)	0.138(2)	−0.0100(9)	−0.010(1)	−0.001(1)
C(21)	2*a*	−0.2258(1)	0.3016(2)	0.0207(1)	0.0394(6)	0.0310(6)	0.0388(7)	0.0006(5)	0.0131(5)	−0.0013(5)
C(22)	2*a*	−0.2228(1)	0.2662(2)	−0.0736(1)	0.0518(8)	0.0490(8)	0.0477(8)	−0.0109(7)	0.0230(6)	−0.0104(7)
C(23)	2*a*	−0.2899(2)	0.1293(3)	−0.1342(1)	0.0610(9)	0.059(1)	0.0524(9)	−0.0113(8)	0.0250(8)	−0.0205(8)
C(24)	2*a*	−0.3623(1)	0.0306(2)	−0.1001(1)	0.0490(8)	0.0440(8)	0.064(1)	−0.0072(7)	0.0149(7)	−0.0162(7)
C(25)	2*a*	−0.4477(1)	−0.0363(3)	0.0299(2)	0.0465(8)	0.050(1)	0.081(1)	−0.0096(7)	0.0201(8)	0.0056(9)
C(26)	2*a*	−0.4588(2)	−0.0024(3)	0.1203(2)	0.0533(9)	0.073(1)	0.080(1)	−0.0132(9)	0.0279(9)	0.020(1)
C(27)	2*a*	−0.3917(2)	0.1325(3)	0.1824(2)	0.0551(9)	0.083(1)	0.054(1)	−0.0017(9)	0.0241(8)	0.0171(9)
C(28)	2*a*	−0.3138(1)	0.2299(3)	0.1531(1)	0.0448(7)	0.058(1)	0.0454(8)	−0.0019(7)	0.0150(6)	0.0061(7)
C(29)	2*a*	−0.3011(1)	0.1992(2)	0.0580(1)	0.0356(6)	0.0348(7)	0.0438(7)	0.0043(5)	0.0119(5)	0.0056(6)
C(30)	2*a*	−0.3705(1)	0.0628(2)	−0.0043(1)	0.0381(7)	0.0372(7)	0.0581(9)	0.0005(5)	0.0143(6)	0.0022(6)
C(31)	2*a*	−0.1543(1)	0.4542(2)	0.0821(1)	0.0407(6)	0.0322(6)	0.0372(6)	0.0020(5)	0.0147(5)	−0.0018(5)
C(32)	2*a*	−0.2082(2)	0.6391(2)	0.0503(2)	0.0542(9)	0.0371(8)	0.078(1)	0.0119(7)	0.0102(8)	−0.0076(8)

Acknowledgments. We thank the National Science Foundation (Bulgaria) and the "Internationales Büro des BMBF bei der DLR" (Germany) for the support of our project BUL-001-96. One of us (T. K.) thanks the Alexander von Humboldt-Stiftung for financial support.

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