Crystal structure of 1,3,5-tribenzoylbenzene, $C_{27}H_{18}O_3$

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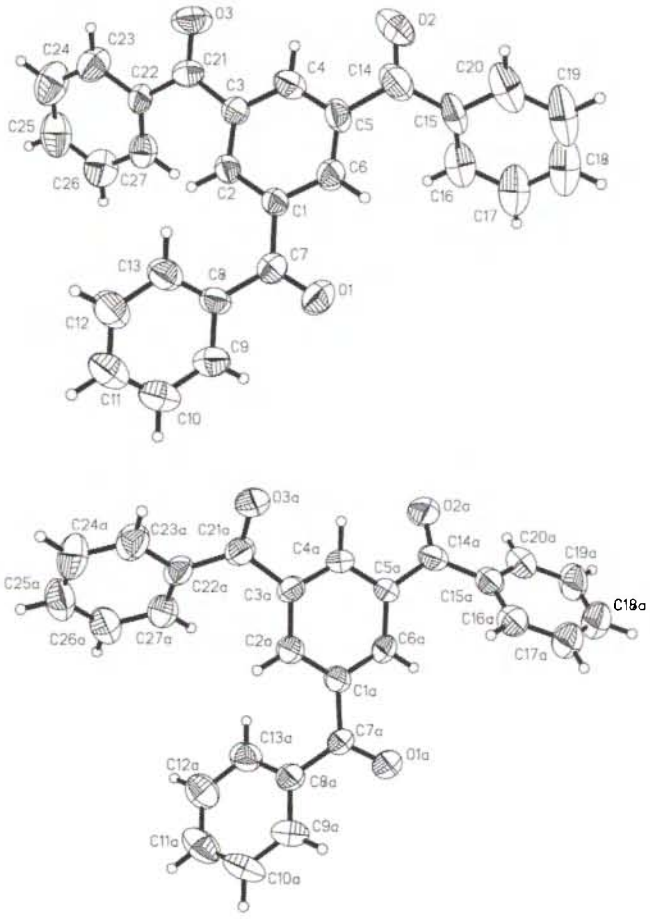

Abstract

$C_{27}H_{18}O_3$, triclinic, $P\bar{1}$ (No. 2), $a = 7.799(2)$ Å, $b = 12.019(2)$ Å, $c = 21.665(3)$ Å, $\alpha = 94.11(2)°$, $\beta = 97.59(2)°$, $\gamma = 91.29(2)°$, $V = 2006.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.080$, $wR(F^2) = 0.130$, $T = 291$ K.

Source of material

The title compound was obtained by heating of 1,3,5-benzenetricarboxylic acid with thionylchlorid - $SOCl_2$ - in the presence of catalytic amounts of dimethylformamide (DMF). The resulting triacyl chloride was isolated and recrystallized from heptane. 1,3,5-Tribenzoylbenzene was synthesized by Friedel-Crafts reaction of the triacylchloride and dry benzene following the procedure of Murray and Trozzolo [1]. The reaction product was recrystallized from ethanol to give colourless crystals of 1,3,5-tribenzoylbenzene (mp 387 K – 389 K). These were sublimated in vacuo and recrystallized two times from anhydrous ethanol to give crystals with a mp in the range 393 K – 394 K. The IR spectrum of the title compound in the solid state shows a doublet at 1662 cm^{-1} – 1654 cm^{-1} whereas the spectrum of the related compound isophthalophenone shows only a single band at 1657 cm^{-1}, therefore in the title compound exist measurable vibrational interactions between the carbonyl groups.

Discussion

The structure determination was undertaken in order to obtain more structural information about 1,3,5-benzenetricarboxylic acid derivatives, which are structurally connected with isophthalic acid and terephthalic acid ones. The similar molecule 1,4-dibenzoylbenzene crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [2]. On the other hand the acceptance of an electron into the first antibonding molecule orbital can easily transform the title compound into the corresponding anion-radical; this is of great interest as an intermediate species in some electrochemical reactions [3-5]. The dihedral angles of the benzoyl fragments with the central phenylene ring are in the range from 129.5(2)° to 137.9(2)° in one molecule and from 50.4(2)° to 135.7(2)° in the other molecule of the asymmetric unit. The bond angles around the C atoms of the carbonyl groups do not deviate significantly from 120°, indicating sp^2 hybridization.

Table 1. Data collection and handling.

Crystal:	colourless column, size 0.05 × 0.10 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.84 cm^{-1}
Diffractometer, scan mode:	Nonius Mach3, ω/2θ
$2\theta_{max}$:	49.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7593, 7030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2482
$N(param)_{refined}$:	541
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL-plus [8], PARST95 [9]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.3951	0.5454	0.3194	0.067
H(4)	2*i*	0.4057	0.7402	0.1781	0.081
H(6)	2*i*	0.2868	0.8679	0.3413	0.075
H(9)	2*i*	0.3795	0.6466	0.5222	0.099
H(10)	2*i*	0.3084	0.4897	0.5702	0.107
H(11)	2*i*	0.1547	0.3426	0.5124	0.112
H(12)	2*i*	0.0725	0.3528	0.4077	0.107
H(13)	2*i*	0.1377	0.5090	0.3588	0.087
H(16)	2*i*	0.4991	1.0014	0.3323	0.118
H(17)	2*i*	0.5205	1.1756	0.3852	0.146
H(18)	2*i*	0.3588	1.3172	0.3458	0.162
H(19)	2*i*	0.1714	1.2878	0.2561	0.155
H(20)	2*i*	0.1474	1.1133	0.2020	0.129
H(23)	2*i*	0.4983	0.3446	0.1415	0.104
H(24)	2*i*	0.6578	0.1933	0.1696	0.131
H(25)	2*i*	0.8196	0.1964	0.2659	0.127
H(26)	2*i*	0.8217	0.3514	0.3361	0.111
H(27)	2*i*	0.6626	0.5040	0.3077	0.084

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2A)	2*i*	–0.1016	0.7089	0.1118	0.071
H(4A)	2*i*	–0.0722	0.6061	0.2839	0.068
H(6A)	2*i*	–0.219	0.9154	0.2526	0.071
H(9A)	2*i*	–0.136	1.0454	0.0468	0.095
H(10A)	2*i*	–0.2269	1.0261	–0.0588	0.125
H(11A)	2*i*	–0.4157	0.8823	–0.1001	0.128
H(12A)	2*i*	–0.5024	0.7517	–0.0374	0.109
H(13A)	2*i*	–0.4006	0.7663	0.0688	0.092
H(16A)	2*i*	0.0096	0.9639	0.3324	0.083
H(17A)	2*i*	0.0361	1.1334	0.3900	0.102
H(18A)	2*i*	–0.1238	1.1656	0.4713	0.118
H(19A)	2*i*	–0.3026	1.0272	0.4973	0.112
H(20A)	2*i*	–0.3270	0.8558	0.4407	0.091
H(23A)	2*i*	0.1208	0.3592	0.1187	0.102
H(24A)	2*i*	0.0507	0.2670	0.0224	0.123
H(25A)	2*i*	–0.1842	0.3186	–0.0449	0.117
H(26A)	2*i*	–0.3503	0.4635	–0.0133	0.106
H(27A)	2*i*	–0.2820	0.5558	0.0847	0.088

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*i*	0.3359(6)	0.7838(3)	0.4419(2)	0.168(4)	0.056(2)	0.071(2)	–0.006(2)	0.057(3)	–0.010(2)
O(2)	2*i*	0.2662(7)	0.9243(3)	0.1687(2)	0.225(6)	0.087(3)	0.073(3)	0.054(3)	0.023(3)	0.039(2)
O(3)	2*i*	0.4245(5)	0.5429(3)	0.1431(2)	0.114(3)	0.092(3)	0.041(2)	0.035(2)	0.014(2)	0.003(2)
O(1A)	2*i*	–0.1681(5)	1.0161(3)	0.1603(1)	0.149(4)	0.040(2)	0.057(2)	0.016(2)	0.004(2)	0.005(2)
O(2A)	2*i*	–0.2103(5)	0.6983(3)	0.3731(1)	0.151(4)	0.056(2)	0.050(2)	0.001(2)	0.025(2)	0.011(2)
O(3A)	2*i*	0.0689(4)	0.4749(2)	0.2151(1)	0.081(3)	0.052(2)	0.060(2)	0.023(2)	0.002(2)	0.010(2)
C(1)	2*i*	0.3312(6)	0.7037(3)	0.3404(2)	0.052(3)	0.038(3)	0.043(3)	0.004(2)	0.016(2)	0.006(2)
C(2)	2*i*	0.3816(6)	0.6149(3)	0.3034(2)	0.056(3)	0.036(3)	0.045(3)	0.008(2)	0.013(2)	0.008(2)
C(3)	2*i*	0.4121(6)	0.6286(3)	0.2426(2)	0.052(3)	0.042(3)	0.042(3)	0.009(2)	0.011(2)	0.003(2)
C(4)	2*i*	0.3881(6)	0.7312(4)	0.2191(2)	0.058(4)	0.059(3)	0.047(3)	0.006(3)	0.011(2)	0.015(2)
C(5)	2*i*	0.3384(6)	0.8212(3)	0.2552(2)	0.058(4)	0.040(3)	0.060(3)	0.013(2)	0.012(3)	0.012(2)
C(6)	2*i*	0.3146(6)	0.8069(3)	0.3161(2)	0.057(3)	0.044(3)	0.051(3)	0.007(2)	0.017(2)	0.002(2)
C(7)	2*i*	0.3120(6)	0.6985(4)	0.4077(2)	0.072(4)	0.047(3)	0.051(3)	0.010(3)	0.018(3)	0.000(3)
C(8)	2*i*	0.2666(6)	0.5943(4)	0.4349(2)	0.061(4)	0.052(3)	0.040(3)	0.013(3)	0.017(3)	0.011(2)
C(9)	2*i*	0.3171(7)	0.5875(4)	0.4989(2)	0.079(4)	0.074(4)	0.049(3)	0.006(3)	0.017(3)	0.004(3)
C(10)	2*i*	0.2748(7)	0.4937(5)	0.5276(2)	0.078(5)	0.088(4)	0.051(3)	0.009(3)	0.013(3)	0.019(3)
C(11)	2*i*	0.1831(8)	0.4060(5)	0.4932(3)	0.082(5)	0.079(4)	0.069(4)	0.009(3)	0.017(3)	0.030(3)
C(12)	2*i*	0.1340(7)	0.4125(4)	0.4308(2)	0.083(4)	0.064(3)	0.069(4)	–0.002(3)	0.010(3)	0.021(3)
C(13)	2*i*	0.1736(6)	0.5057(4)	0.4013(2)	0.066(4)	0.059(3)	0.051(3)	0.011(3)	0.010(3)	0.015(3)
C(14)	2*i*	0.3072(8)	0.9287(4)	0.2250(3)	0.096(5)	0.065(4)	0.074(4)	0.016(3)	0.019(3)	0.028(3)
C(15)	2*i*	0.3215(7)	1.0374(4)	0.2617(3)	0.070(4)	0.040(3)	0.091(4)	0.011(3)	0.030(3)	0.029(3)
C(16)	2*i*	0.4321(8)	1.0585(4)	0.3164(3)	0.070(5)	0.056(4)	0.114(5)	0.008(3)	0.018(4)	0.017(3)
C(17)	2*i*	0.4457(9)	1.1628(5)	0.3481(3)	0.094(5)	0.053(4)	0.145(6)	0.002(4)	0.021(4)	0.004(4)
C(18)	2*i*	0.349(1)	1.2468(5)	0.3246(4)	0.092(6)	0.054(4)	0.185(8)	0.008(4)	0.042(5)	0.008(5)
C(19)	2*i*	0.2376(9)	1.2298(5)	0.2712(4)	0.082(6)	0.049(4)	0.194(8)	0.017(4)	0.057(5)	0.039(5)
C(20)	2*i*	0.2231(7)	1.1251(5)	0.2390(3)	0.072(5)	0.068(4)	0.128(5)	0.017(3)	0.028(4)	0.045(4)
C(21)	2*i*	0.4629(7)	0.5359(4)	0.1992(2)	0.068(4)	0.057(3)	0.041(3)	0.003(3)	0.017(3)	0.002(2)
C(22)	2*i*	0.5621(6)	0.4393(3)	0.2221(2)	0.063(4)	0.034(3)	0.050(3)	0.005(2)	0.014(3)	–0.003(2)
C(23)	2*i*	0.5629(7)	0.3461(4)	0.1808(2)	0.073(4)	0.063(3)	0.068(3)	0.007(3)	0.004(3)	–0.009(3)
C(24)	2*i*	0.6587(8)	0.2558(4)	0.1975(3)	0.077(5)	0.067(4)	0.114(5)	0.020(4)	0.007(4)	–0.017(4)
C(25)	2*i*	0.7548(8)	0.2576(4)	0.2549(3)	0.067(5)	0.057(4)	0.130(5)	0.018(3)	0.009(4)	0.009(4)
C(26)	2*i*	0.7566(7)	0.3504(4)	0.2968(3)	0.059(4)	0.072(4)	0.089(4)	0.009(3)	0.000(3)	0.005(3)
C(27)	2*i*	0.6607(6)	0.4411(4)	0.2799(2)	0.051(4)	0.048(3)	0.070(4)	0.006(3)	0.015(3)	0.000(3)
C(1A)	2*i*	–0.1665(6)	0.8268(3)	0.1753(2)	0.060(4)	0.043(3)	0.038(3)	0.012(2)	0.008(2)	0.005(2)
C(2A)	2*i*	–0.1143(6)	0.7224(3)	0.1537(2)	0.057(3)	0.045(3)	0.042(3)	0.012(2)	0.009(2)	0.003(2)
C(3A)	2*i*	–0.0809(6)	0.6380(3)	0.1944(2)	0.048(3)	0.034(2)	0.048(3)	0.002(2)	0.007(2)	0.005(2)
C(4A)	2*i*	–0.0972(6)	0.6613(3)	0.2564(2)	0.057(3)	0.035(3)	0.043(3)	0.005(2)	0.003(2)	0.012(2)
C(5A)	2*i*	–0.1493(6)	0.7638(3)	0.2796(2)	0.056(3)	0.041(3)	0.032(3)	0.004(2)	0.002(2)	0.006(2)
C(6A)	2*i*	–0.1838(6)	0.8461(3)	0.2380(2)	0.057(3)	0.035(3)	0.048(3)	0.009(2)	0.007(2)	–0.004(2)
C(7A)	2*i*	–0.1957(6)	0.9215(4)	0.1357(2)	0.078(4)	0.033(3)	0.048(3)	0.011(2)	0.010(3)	0.004(2)
C(8A)	2*i*	–0.2537(7)	0.9061(4)	0.0682(2)	0.065(4)	0.041(3)	0.049(3)	0.018(3)	0.010(3)	0.006(2)
C(9A)	2*i*	–0.2070(6)	0.9846(4)	0.0299(2)	0.070(4)	0.064(3)	0.060(3)	0.004(3)	0.010(3)	0.027(3)
C(10A)	2*i*	–0.2638(8)	0.9745(5)	–0.0330(2)	0.101(5)	0.102(5)	0.052(4)	0.007(4)	0.010(4)	0.038(3)
C(11A)	2*i*	–0.3750(9)	0.8881(6)	–0.0576(3)	0.089(5)	0.117(5)	0.049(3)	0.019(4)	–0.005(3)	0.020(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12A)	2*i*	–0.4269(7)	0.8102(5)	–0.0204(2)	0.065(4)	0.089(4)	0.061(4)	0.003(3)	0.002(3)	0.006(3)
C(13A)	2*i*	–0.3659(7)	0.8191(4)	0.0432(2)	0.071(4)	0.062(3)	0.054(3)	0.018(3)	0.014(3)	0.012(3)
C(14A)	2*i*	–0.1749(6)	0.7802(4)	0.3461(2)	0.074(4)	0.054(3)	0.041(3)	0.012(3)	0.007(3)	0.012(2)
C(15A)	2*i*	–0.1609(6)	0.8919(4)	0.3802(2)	0.056(4)	0.054(3)	0.041(3)	0.012(3)	0.006(2)	0.004(2)
C(16A)	2*i*	–0.0534(6)	0.9760(4)	0.3657(2)	0.057(4)	0.058(3)	0.053(3)	0.013(3)	0.008(3)	0.004(3)
C(17A)	2*i*	–0.0380(7)	1.0776(4)	0.3999(2)	0.074(4)	0.060(3)	0.070(4)	0.004(3)	0.013(3)	–0.005(3)
C(18A)	2*i*	–0.1327(8)	1.0965(5)	0.4487(3)	0.096(5)	0.060(4)	0.075(4)	0.004(3)	0.005(4)	–0.013(3)
C(19A)	2*i*	–0.2397(8)	1.0142(5)	0.4640(2)	0.094(5)	0.071(4)	0.059(3)	0.017(3)	0.016(3)	–0.017(3)
C(20A)	2*i*	–0.2544(6)	0.9118(4)	0.4301(2)	0.061(4)	0.073(4)	0.048(3)	0.005(3)	0.005(3)	0.005(3)
C(21A)	2*i*	–0.0203(6)	0.5229(3)	0.1752(2)	0.053(3)	0.041(3)	0.051(3)	0.005(2)	0.010(2)	0.006(2)
C(22A)	2*i*	–0.0697(6)	0.4696(3)	0.1116(2)	0.055(4)	0.038(3)	0.055(3)	0.010(2)	0.016(3)	0.002(2)
C(23A)	2*i*	0.0261(7)	0.3812(4)	0.0922(2)	0.072(4)	0.058(3)	0.076(4)	0.015(3)	0.019(3)	–0.003(3)
C(24A)	2*i*	–0.0161(8)	0.3257(4)	0.0345(3)	0.083(5)	0.074(4)	0.088(4)	0.018(4)	0.025(4)	–0.023(3)
C(25A)	2*i*	–0.1564(8)	0.3559(5)	–0.0056(3)	0.091(5)	0.083(4)	0.061(4)	–0.009(4)	0.027(4)	–0.014(3)
C(26A)	2*i*	–0.2550(7)	0.4424(4)	0.0134(2)	0.080(4)	0.078(4)	0.053(3)	0.001(3)	0.010(3)	–0.004(3)
C(27A)	2*i*	–0.2132(7)	0.4985(4)	0.0721(2)	0.061(4)	0.056(3)	0.059(3)	0.011(3)	0.014(3)	0.000(3)

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References

1. Murray, R. W.; Trozzolo, A.: Dicarbenes. The Preparation and some Reactions of 1,4-Bis(α-diazobenzyl)benzene. J. Org. Chem. **26** (1961) 3109-3112.
2. Kolev, T.; Preut, H.; Bleckmann, P.; Juchnovski, I.: 1-4-Dibenzoylbenzene. Acta Crystallogr. C**48** (1992) 1715-1717.
3. Kolev, T.: Using of IR Spectroscopy for Investigation of Organic Compounds and Negative Charged Ions Containing Carbonyl Groups. PhD thesis. Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria 1982.
4. Svaan, M.; Parker, V.: Temperature Effects on Electrode Processes VII. The Effects of Solvent and Electrolyte on the Relative Entropies of Formation of Doubly and Singly Charged Ions of Organic Compounds. Acta Chem. Scand. Ser. B **38** (1984) 767-771.
5. Juchnovski, I.; Kolev, T.: Infrared Spectra and Structures of the Anion-Radicals of Substituted Benzophenones. Spectrsc. Lett. **18** (1985) 481-490
6. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.
8. Sheldrick, G. M.: SHELXTL-Plus. Release 4.1 Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1991.
9. Nardelli, M.: A system of Fortran routines for calculating molecular structure parameters from the results of crystal structure analyses. J. Appl. Crystallogr. **28** (1995) 659.