Acta Chemica Scandinavica, 1998: 52: 1006–1009
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Crystal Structure of the 1:1 Complex Between Mesitylene and Fluoranil. Analysis of Stacking Interactions in Complexes Containing Fluoranil

Tor Dahl

Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

Dahl, T., 1998. Crystal Structure of the 1:1 Complex Between Mesitylene and Fluoranil. Analysis of Stacking Interactions in Complexes Containing Fluoranil. Acta Chem. Scand. 52: 1006–1009. © Acta Chemica Scandinavica 1998.

The title compound crystallizes in the monoclinic space group $P2_1/m$ with cell dimensions $a=6.849(2)$, $b=13.452(2)$, $c=8.072(2)$ Å, $\beta=103.95(2)°$. All data were collected from a twinned crystal, and the structure was refined to $R=0.074$. 306 observed reflections were included in the refinement. The partner molecules are stacked alternately with an interplanar distance of 3.421(4) Å. The observed bond distances and angles in fluoranil indicate some orientational disorder of this molecule.

This and six other complexes containing fluoranil have been included in a molecular-packing analysis, based on atom-to-atom potential lattice-energy calculations. The analysis shows that charge-transfer interactions have effects on the interplanar distances in all the complexes. These effects are to some extent correlated with the ionization potentials of the donor molecules. The results indicate that the interactions are of a different kind in the complex with *N,N*-dimethylaniline than in the other complexes.

Information about the nature of intermolecular interactions in the crystalline state may be obtained by molecular-packing analysis of crystal stuctures of closely related compounds.[1] Structures of the molecular complexes of fluoranil with durene[2] and hexamethylbenzene[3] have been included in an earlier analysis which was mainly concentrated on hexafluorobenzene complexes.[1] Structures of fluoranil complexes with perylene,[4] pyrene,[5] chrysene,[6] and *N,N*-dimethylaniline[7] are also known. A molecular-packing analysis of a series of fluoranil complexes with partner molecules which differ in donor strength and bulkiness may elucidate the effect of charge transfer on the intermolecular interactions in this kind of complex. In order to obtain a more comprehensive analysis, it would be desirable to include more complexes with methylated benzenes. Complexes with 1,2-dimethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene and pentamethylbenzene have been crystallized, but the stuctures seem to be so disordered at room temperature that no structure determination has been performed. Preliminary crystallographic investigations of the mesitylene complex indicated no disorder. The crystal structure of this complex was therefore determined. Although the preliminary investigations indicated large thermal vibrations, no attempt at cooling the crystals was made, as the structures of the other complexes in this series have been determined from room-temperature data.

Experimental

Needle-shaped, light yellow crystals of the mesitylene–fluoranil complex were obtained by slow evaporation of the excess solvent from a solution of fluoranil in mesitylene. They were all twinned crystals with (100) as twin plane. The cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer. The crystals were kept in sealed capillaries, and Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) was used. The cell parameters were obtained from the setting angles of 25 reflections. Crystal data and experimental conditions are given in Table 1. Corrections were made for a continous reductions of the standard reflections down to 91% of their original intensities, for Lorentz and polarization effects and for absorption, using Gaussian integration.

All non-H atoms were found by direct methods using SIMPEL83.[8] The H atoms could not be observed in a difference map. Their positions were calculated, assuming C–H distances of 0.95 Å and orientational disorder of those belonging to methyl groups. During the least-squares refinement the H atoms were assumed to ride on the C atoms to which they are bonded, and to have isotropic U-values, 1.3 times U_{eq} of the C atoms.

All $0kl$-reflections from different individuals of the twinned crystal overlap exactly. A separate scale factor, 66% of that for the other reflections, was estimated for these reflections during the refinement. Each pair of

Table 1. Crystal data and experimental conditions.

Compound	Mesitylene–Fluoranil
Formula	$C_9H_{12} \cdot C_6F_4O_2$
M_r	300.25
Crystal system	Monoclinic
Space group	$P2_1/m$
a/Å	6.849(2)
b/Å	13.452(2)
c/Å	8.072(2)
β/°	103.95(2)
V/Å^3	721.8(3)
Z	2
D_x/g cm^{-3}	1.382
Wavelength (Cu $K\alpha$)/Å	1.5418
μ(Cu $K\alpha$)/cm^{-1}	10.71
Absorption transmission factor (max/min)	0.9375/0.7802
Crystal dimensions/mm	$0.75 \times 0.25 \times 0.12$
Scan mode	$\omega/2\Theta$
Scan speed of ω/° min^{-1}	0.5–1.6
Θ range/°	0–70
Criterion for significance	$I > 2\sigma(I)$
No. of independent reflections measured	1288
No. of reflections used in final refinement	306
w=for $\|F_o\| < 28$	1.0
w=for $\|F_o\| > 28$	$(28/F_o)^2$
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F\|$	0.074
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF^2]^{1/2}$	0.076
Max $\Delta\rho$/e Å^{-3}	0.35

reflections $(2, k, l)$ and $(2, k, -l-1)$, $(4, k, l)$ and $(4, k, -l-2)$, and $(6, k, l)$ and $(6, k, -l-3)$ from different individuals are very close together in the reciprocal lattice. During the refinement it became clear that the intensities of the reflections (200), (20–1), (210), (21–1), (400), (40–2) and (40–1) were strongly influenced by overlap from the other individual. In addition, the reflection with the lowest Θ-value, (001), seemed to have systematic errors. All these reflections were omitted in the final refinement. Final positional parameters and U_{eq}-values for the non-H atoms are shown in Table 2.

Table 2. Positional parameters and equivalent temperature factors (in Å^2) for non-H atoms.[a]

Atom	x	y	z	U_{eq}[b]
F(1)	0.2486(11)	0.1510(6)	0.0624(8)	0.170(3)
F(2)	0.3887(12)	0.1508(7)	0.6541(9)	0.229(4)
O(1)	0.3123(13)	0.0502(5)	0.3539(12)	0.163(3)
C(1)	0.2833(13)	0.1980(6)	0.2062(11)	0.096(4)
C(2)	0.3171(15)	0.1423(7)	0.3567(12)	0.099(4)
C(3)	0.3548(14)	0.1978(8)	0.5105(11)	0.120(5)
C(4)	0.7654(17)	0.250	0.1487(15)	0.084(5)
C(5)	0.7891(13)	0.1596(7)	0.2356(10)	0.080(3)
C(6)	0.8279(13)	0.1602(7)	0.4065(11)	0.091(4)
C(7)	0.8489(19)	0.250	0.4927(15)	0.089(5)
C(8)	0.7637(16)	0.0642(8)	0.1356(14)	0.152(5)
C(9)	0.8933(25)	0.250	0.6887(18)	0.165(9)

[a] Standard deviations in parentheses.
[b] $U_{eq} = 1/3\Sigma\Sigma U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$.

Bond distances and angles not involving H atoms are shown in Fig. 1. Lists of observed and calculated structure factors, anisotropic temperature factors and positions and U_{iso}-values for the H atoms may be obtained from the author on request.

All computer programs used in the structure determination and refinement are included in Ref. 9. Scattering factors were taken from Ref. 10.

Results

No bond distances or angles in the mesitylene molecule (Fig. 1b) deviate significantly from those expected. The observed symmetry of the fluoranil molecule (Fig. 1a) is, however, somewhat closer to hexagonal than that observed in the pure compound[11] and in some of its other complexes.[4–6] This indicates some orientational disorder of this molecule. A similar, but less pronounced effect was observed for the durene complex.[2] No atoms of the fluoranil molecule or non-H atoms of the mesitylene molecule deviate significantly from least-squares planes through the molecules.

The molecular packing is shown in Fig. 2. The partner molecules are stacked alternately in infinite columns. The angle between the molecular planes is not significantly different from zero, and the angles between these planes and the stack axis are not significantly different from 90°. The molecular overlap and the interplanar distance are approximately the same on both sides of the molecules. The overlap is not very different from that of the mesitylene–hexafluorobenzene complex.[12] The mean value of the interplanar distances, 3.421(4) Å, is 0.14 Å shorter than that in the hexafluorobenzene complex, but still relatively long compared to that usually observed in charge transfer complexes. As in the hexafluorobenzene complex an intermolecular $CH_3 \cdots F$ contact (indicated in Fig. 2) seems to be important. The $C(8) \cdots F(1)$ distance is 3.298(13) Å, 0.06 Å longer than the corresponding distance in the hexafluorobenzene complex, and the angle $C(5)–C(8) \cdots F(1)$ is 175(5)°.

Molecular-packing analysis of fluoranil complexes

The molecular packing was analyzed by atom-to-atom lattice energy calculations, using the computer program PCK83.[13] The parameters A_{jk}, B_{jk} and C_{jk} in the energy expression

$$E = \sum_j \sum_k -A_{jk} r_{jk}^{-6} + B_{jk} \exp(-C_{jk} r_{jk}) + q_j q_k r_{jk}^{-1}$$

are those by Williams *et al.*,[14–16] and the net atomic charges q were calculated for the individual molecules by the AM1 method,[17] using the computer program GAUSSIAN 86.[18]

This analysis was carried out mainly in order to elucidate the following questions: Has the charge-transfer interaction any effect even on the relatively long interplanar distance in the fluoranil complex with mesi-

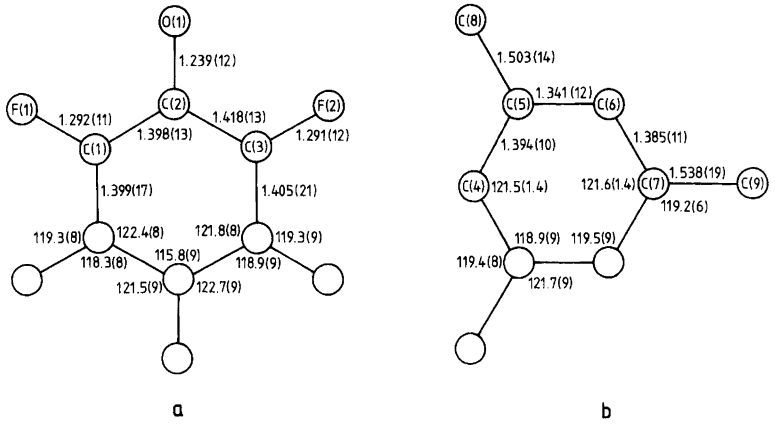

Fig. 1. Bond distances (in Å) and angles (in °) in fluoranil (a) and mesitylene (b).

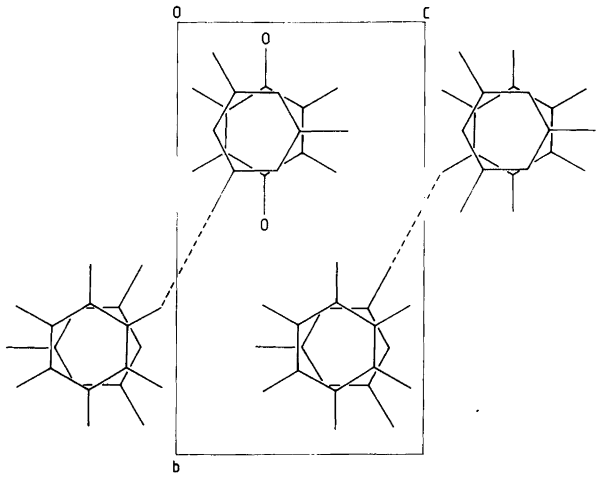

Fig. 2. The molecular packing, viewed down the *a*-axis. The short $CH_3 \cdots F$ contact is shown with a dotted line.

tylene, which is known to be a relatively weak electron donor? How much do the charge transfer interactions influence the interplanar distance in other fluoranil complexes? How strongly is this influence correlated with the vertical ionization potential of the donor molecule, which is regarded as a measure of its donor strength?[19]

In order to answer these questions it may be useful to minimize the calculated lattice energy by starting with the experimental structure and varying only the crystallographic axes. In the 'optimum density structure' obtained in this way the molecular overlap is the same as in the experimental structure, and the interplanar distance is that expected with this overlap at a temperature of 0 K, if only interactions included in the analytical potentials were present. An increase in the stack axis during this packing-density optimization, which is proportional to the increase in the interplanar distance, is an indication of stronger stacking interactions than those included in the analytical potentials. In this type of complexes this is probably mainly a result of charge transfer interactions. Because of the effect of thermal vibrations at room temperature, the results may indicate such kinds of interactions even when there is a small decrease in the stack axis, substantially smaller than in the other axes.

The relative shifts in the crystallographic axes during packing-density optimizations for the complexes with methylated benzenes and polyaromatic hydrocarbons are shown in Table 3. In these calculations all C–H distances have been adjusted to be 1.00 Å, as the calculation of potential parameters for H atoms was based on a slight foreshortening of the bond distance.[14] Also the structure at −50 °C of the hexamethylbenzene complex has been included in the table. This complex has a disordered structure with two non-equivalent sets of orientations of the fluoranil molecule both at this temperature and at room temperature,[3] and the shifts for this complex have been calculated as weighted mean values for the two

Table 3. Shifts in crystallographic axes (in %) in the packing-density optimizations of complexes of fluoranil with methylated benzenes and polyaromatic hydrocarbons.[a]

Compound	Δa_1	Δa_2	Δa_3	Dist.	Ip
Mesitylene–fluoranil	+0.1	−2.5	−1.4	3.42	8.42[a]
Durene–fluoranil	+1.8	−4.0	−0.9	3.38	8.10[a]
Hexamethylbenzene–fluoranil (room temp.)	+2.9	−2.5	−1.8	3.36	7.86[a]
Hexamethylbenzene–fluoranil (−50 °C)	+3.6	−1.7	−0.8	3.32	7.86[a]
Chrysene–fluoranil	+2.9	−0.8	−0.2	3.23	7.60[b]
Pyrene–fluoranil	+2.1	−0.9	−0.6	3.28	7.41[b]
Perylene–fluoranil	+3.7	−0.8	−0.4	3.23	7.00[b]

[a] a_1 is the stack axis, a_3 is the longest axis. Included in the table are also interplanar distances (in Å) and vertical ionization potentials (in eV) of the donor molecules. [b] Ref. 21. [c] Ref. 22.

orientations. The kind of disorder which probably exists in the mesitylene and the durene complex has been assumed to have negligible effects on the shifts. Also the experimental interplanar distances and the vertical ionization potentials of the donor molecules are included in the table.

Table 3 shows clearly that the charge-transfer interactions have a considerable effect on the length of the stack axis and thus on the interplanar distance even for the complex with mesitylene. Although the increase in the stack axis is very small for this complex, it is 2% larger than the average value for the two other axes. Among the two other axes the decrease is smallest for the axis along which the short $CH_3 \cdots F$ contacts run. A similar effect of the $CH_3 \cdots F$ contact was observed for the mesitylene–hexafluorobenzene complex.[1]

For the other complexes included in Table 3 the difference between the shift in the stack axis and the average shift in the other axes are somewhat larger, ranging from 3 to 5%. For the complexes of methylated benzenes at room temperature there is a nearly linear relationship between the increase in the stack axis and the ionization potential of the electron donor. For the complexes of the polyaromatic hydrocarbons the correlation is not so good, as the increase for the pyrene complex is smaller than for the chrysene complex. The possibillity that the molecular overlap in the pyrene complex, as a result of other kinds of interactions, is somewhat unfavourable for the transfer of charge may be worth a further investigation. The effects of charge transfer interactions on the interplanar distances seem to be approximately the same for the complexes with methylated benzenes as for the complexes with polyaromatic hydrocarbons, in spite of the lower ionization potentials of the latter donors. This observation is not surprising, as the methyl groups may be assumed to form a 'softer' surface, so that the molecules in these complexes can more easily be pressed together.

For the *N,N*-dimethylaniline complex the energy minimization was done in a slightly different way, and the results are therefore not included in Table 3. This complex is very unsymmetric, with a much smaller interplanar distance on the lone-pair side of the amino group than on the other side. In order to treat the two sides individually, a translation of the *N,N*-dimethylaniline molecule along the stack axis was allowed in addition to the variation of the crystallographic axes. This resulted in an increase in the interplanar distance on the lone pair side from 3.24 to 3.50 Å, which is 8.1%, whereas the distance on the other side remained unchanged, 3.46 Å. The other axes both decreased by approximately 2%. A vertical ionization potential of 7.51 eV has been found for this donor by photoelectron spectroscopic investigations.[20] These investigations also show that the highest occupied orbital is a π-orbital. This complex should therefore be expected to be of the same kind as the others in this series. The results of the molecular-packing analysis for this complex differ, however, so much from those obtained for the other complexes that the interactions seem to be of a different kind.

References

1. Dahl, T. *Acta Crystallogr., Sect. B 46* (1990) 283.
2. Dahl, T. and Sørensen, B. *Acta Chem. Scand., Ser. B 39* (1985) 423.
3. Dahl, T. *Acta Chem. Scand. 44* (1990) 56.
4. Hanson, A. W. *Acta Crystallogr. 16* (1963) 1147.
5. Bernstein, J. and Regev, H. *Cryst. Struct. Commun. 9* (1980) 581.
6. Munnoch, P. J. and Wright, J. D. *J. Chem. Soc., Perkin Trans. 2* (1975) 1071.
7. Dahl, T. *Acta Chem. Scand., Ser. A 35* (1981) 701.
8. Schenk, H. and Kiers, C. T. In: Shieldrick, G. M., Kruger, C. and Goddard, R., Eds., *Crystallographic Computing*, Clarendon Press, Oxford 1983, p. 200.
9. *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft 1990.
10. *International Tables for X-Ray Crystallography*. Kynoch Press, Birmingham 1974, Vol. 4, p. 99.
11. Hagen, K., Nicholson, D. G. and Sæthre, L. J. *Acta Crystallogr., Sect. C. 43* (1987) 1959.
12. Dahl, T. *Acta Chem. Scand. 25* (1971) 1031.
13. Williams, D. E. *PCK83: A Crystal Molecular Packing Analysis Program*, University of Louisville, Louisville, KT 1983; Quantum Chemistry Program Exhange, Program No. 481, Department of Chemistry, Indiana University, IN 1983.
14. Williams, D. E. and Cox, S. R. *Acta Crystallogr., Sect. B 40* (1984) 404.
15. Cox, S. R., Hsu, L. Y. and Williams, D. E. *Acta Crystallogr., Sect. A 37* (1981) 293.
16. Hsu, L. Y. and Williams, D. E. *Acta Crystallogr., Sect. A 36* (1980) 277.
17. Dewar, M. J. S., Zoebish, E. G., Healy, E. F. and Stewart, J. J. P. *J. Am. Chem. Soc. 107* (1985) 3902.
18. Frisch, M. J., Brinkley, J. S., Schlegel, H. B., Raghaavachari, K., Melius, C. F., Martin, L., Stewart, J. J. P., Bobrowicz, F. W., Rohlfing, C. M., Kahn, L. R., de Frees, D. J., Seeger, R. A., Whiteside, R. A., Fox, D. J., Fleuder, E. M. and Pople, J. A. *GAUSSIAN 86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburg, PA 1984.
19. Mulliken, R. S. *J. Chim. Phys. 61* (1964) 20.
20. Baker, A. D., May, D. P. and Turner, D. W. *J. Chem. Soc. B* (1968) 22.
21. Maier, J. P. and Heilbronner, E. *Electron Spectroscopy: Theory, Techniques and Applications*, Academic Press, London 1976.
22. Boschi, R., Clar, E. and Schmidt, W. *J. Chem. Phys. 60* (1974) 4406.

Received December 3, 1997.