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A Reconsideration of Fourier Methods for the Refinement of Crystal Structures

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Experience shows that Fourier refinement may be less sensitive to large systematic errors than least-squares methods. A simple procedure, allowing also for the series termination effect, is derived for the refinement of temperature parameters and atomic scale factors (occupancy factors) from geometrical considerations about the shapes of peaks in 'partial F_o and F_c syntheses' (which involve only one atom per unit cell at a time). Low temperature neutron-diffraction data for decaborane [Tippe & Hamilton. (1969). *Inorg. Chem.* **8**, 464] were used to test this procedure and compare its results with those obtained by least-squares methods. An application to the X-ray data of all-*trans*-cyclododeca-1,5,9-triene-nickel, containing various types of systematic errors, is also discussed in detail. It suggests stronger π-complex bonds in that compound than had been expected on the basis of an earlier two-dimensional study.

The refinement of crystal structures is achieved most reliably by least-squares methods, if the measurements are not affected much by systematic errors. In the latter case, however, it may be better to use geometrical criteria in direct space for the fit of the model to the data. This is confirmed by the well known fact that in this case refinement by difference maps often results in more sensible positional parameters (*e.g.* Dierks & Dietrich, 1965; Uttech & Dietrich, 1965).

It is unusual, however, to determine or refine vibrational parameters of atoms by means of Fourier methods, although Cruickshank (1956) developed a set of formulae long ago. These are based on sets of linear equations for the difference density function $D=\varrho_o-\varrho_c$ and its second derivatives at the atomic positions. Including the correction of atomic scale factors, they involve 29 summations per atom.

In the following more geometrical approach this number could be reduced to 13 summations per atom. Three more are needed to correct the positional parameters as well. As in Cruickshank's procedure, interactions between atoms have to be neglected. Automatically adjusted damping factors are therefore applied.

In order to isolate the atomic peaks in Fourier syntheses as completely as possible, two 'partial syntheses', ϱ_c^* and ϱ_o^*, are introduced. They represent only one single atom at a time in the unit cell, namely the atom under consideration:

$$\varrho_c^*(\mathbf{y})\equiv\frac{2}{V}\sum_{\mathbf{h}^*}f(\mathbf{h})q(\mathbf{h})\cos 2\pi\mathbf{hy}$$

$$\varrho_o^*(\mathbf{y})\equiv\varrho_c^*(\mathbf{y})+D$$

where

$$q(\mathbf{h})=\exp\left(-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j\right)$$

and the summation $\mathbf{h}^*$ includes systematic extinctions and extends over one hemisphere in reciprocal space, whose radius is determined by the measurements. $\mathbf{y}$ defines fractional crystal coordinates centred at the atom; the symbol $\mathbf{x}$ is used for coordinates referring to the cell origin. ϱ_c^* will in any case have a well resolved peak, and so will ϱ_o^*, provided the difference synthesis D does agree with it. Whereas in normal F syntheses the resolution of peaks is reduced by the overlap of neighbour atoms (essentially due to the series termination effect), so that light atoms are often unresolved in the neighbourhood of heavy ones, the appearance of the ϱ_o^* peak depends only on the difference synthesis D, which is approximately free of series termination effect. Therefore sections through ϱ_o^* peaks should also be useful for the representation of crystal structures containing atoms of very different scattering power.

It can be assumed that the peaks of ϱ_c^* and ϱ_o^* syntheses near their centres should be very well approximated by an anisotropic smearing function as developed by Cruickshank (1956) for harmonic vibrations. Introducing a proportionality factor C and an atomic scale factor G (occupancy factor), which may also be used for refinement of the scattering factor, one obtains for the ϱ_c^* peak

$$\varrho_c^*(\mathbf{y})=G_cC(\det\mathbf{V}_c^{-1})^{1/2}\exp\left(-\tfrac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3}V_{cij}^{-1}y_iy_j\right)\quad(1)$$

and for its centre ($\mathbf{y}=0$)

$$\varrho_c^*(0)=G_cC(\det\mathbf{V}_c^{-1})^{1/2}.\quad(2)$$

$\mathbf{V}_c^{-1}$ and C include not only the atomic vibrations but also the series termination effect and, in the case of X-ray measurements, the electron distribution close to the atomic nucleus. Each of these effects should be formally describable as atomic vibrations. Therefore the tensor $\mathbf{V}_c$, appearing in the exponent of the transform of the smearing function (Cruickshank, 1956; Scheringer, 1966), should be composed of additive contributions of the vibration tensor $\boldsymbol{\beta}$ and similar tensors referring to the electron density distribution near the nucleus and to the series termination effect. As the latter two contributions can be set equal for ϱ_c^* and ϱ_o^*, the correction for β_{ij} becomes simply

$$\Delta\beta_{ij}=2\pi^2(V_{oij}-V_{cij})\,. \tag{3}$$

So these corrections can be traced back to the inverse tensors $\mathbf{V}_o^{-1}$ and $\mathbf{V}_c^{-1}$, which are available from the peak shape. For $\mathbf{V}_c^{-1}$ one obtains from (1) and (2) by differentiation at the atomic centre

$$V_{cij}^{-1}=-\frac{1}{\varrho_c^*(0)}\left(\frac{\partial^2\varrho_c^*}{\partial y_i\partial y_j}\right)_{\mathbf{y}=0} \tag{4}$$

which can be evaluated by the summations

$$\varrho_c^*(0)=\frac{2}{V}G_c\sum_{\mathbf{h}*}f(\mathbf{h})q(\mathbf{h}) \tag{5}$$

$$\left(\frac{\partial^2\varrho_c^*}{\partial y_i\partial y_j}\right)_{\mathbf{y}=0}=-4\pi^2\frac{2}{V}\sum_{\mathbf{h}*}h_ih_jf(\mathbf{h})q(\mathbf{h}) \tag{6}$$

where $f(\mathbf{h})$ is the scattering and $q(\mathbf{h})$ the temperature factor of the atom for reflexion $\mathbf{h}$.

For the representation of ϱ_o^* the smearing function of type (1) has to be modified by an additive term U, mainly because of the errors in the low-order reflexions

$$\varrho_c^*(\mathbf{y})=U+G_oC(\det\mathbf{V}_o^{-1})\times\exp\left(-\tfrac{1}{2}\sum_i\sum_j V_{oij}^{-1}y_iy_j\right). \tag{7}$$

U then becomes equal to D at the end of the refinement.

Using (2) and the determinant d_o^{-1}, which is available from the second derivatives at the ϱ_o^* peak,

$$d_o^{-1}=\det\left[\frac{G_o}{G_c}\left(\frac{\det\mathbf{V}_o^{-1}}{\det\mathbf{V}_c^{-1}}\right)^{1/2}\mathbf{V}_o^{-1}\right]=\left(\frac{G_o}{G_c}\right)^3\frac{(\det\mathbf{V}_o^{-1})^{5/2}}{(\det\mathbf{V}_c^{-1})^{3/2}} \tag{8}$$

one obtains for V_{oij}^{-1}

$$V_{oij}^{-1}=-\left(\frac{G_c}{G_o}\right)^{2/5}\left(\frac{\det\mathbf{V}_c^{-1}}{d_o^{-1}}\right)^{1/5}\frac{1}{\varrho_c^*(0)}\left(\frac{\partial^2\varrho_o^*}{\partial y_i\partial y_j}\right)_{\mathbf{y}=0}. \tag{9}$$

When the scale factor for the reflexion data is determined independently, the coefficient $\left(\frac{G_c}{G_o}\right)^{2/5}$ may be set approximately equal to one. If G is not to be refined this is exact. Otherwise it will result in an interaction of the temperature parameters with the atomic scale factor G.

For the correction of G one obtains from (2), (7) and (8)

$$\Delta G=G_o-G_c=G_c\left[\left(\frac{\varrho_o^*-U}{\varrho_c^*}\right)_{\mathbf{y}=0}^{5/2}\left(\frac{d_o^{-1}}{\det\mathbf{V}_c^{-1}}\right)^{-1/2}-1\right]. \tag{10}$$

Here U has to be neglected, which will lead to an error in G.

The second derivatives of $\varrho_o^*(0)$ can be approximated by calculating the second derivatives of D at the atomic positions

$$\left(\frac{\partial^2D}{\partial y_i\partial y_j}\right)_{\mathbf{y}=0}=-4\pi^2\frac{2}{V}\sum_{\mathbf{h}}h_ih_j[(A_o-A_c)\cos2\pi\mathbf{hx}+(B_o-B_c)\sin2\pi\mathbf{hx}]_{\mathbf{y}=0} \tag{11}$$

and adding them to the corresponding derivatives (6) of $\varrho_c^*(0)$. This of course affords the ϱ_o^* peak to be very nearly at the same place as the ϱ_c^* peak. In practice this can be secured by a damping factor, computed from the atomic shift. The same damping factor can be used for manipulation of the refinement of atomic scale factors G.

The positional shifts Δx_i are calculated according to Lipson & Cochran (1953) from the three equations

$$\left.\sum_j\left(\frac{\partial^2\varrho_c^*}{\partial y_i\partial y_j}\right)_{\mathbf{y}=0}\cdot\Delta x_j=\left(\frac{\partial D}{\partial x_i}\right)_{\mathbf{y}=0}\right\}i=1,2,3$$

for whose solution the matrix $\mathbf{V}_c$ can again be used:

$$\Delta x_j=\frac{1}{\varrho_c^*(0)}\sum_i V_{cij}\left(\frac{\partial D}{\partial x_i}\right)_{\mathbf{y}=0}.$$

For the independent scaling of the F_o's a Fourier procedure proved best. It was based on the criterion that the average value of D at the atomic centres should be zero, whereas at individual centres D may be non-zero according to (7).

For atoms for which only an isotropic vibration parameter B is to be refined, one can compute $\Delta\boldsymbol{\beta}$ as shown above and determine the isotropic mean correction ΔB according to Hamilton (1959).

In order to reduce the interaction of strong scatterers on weaker ones, for each atom the ratio of its effective scattering power $|Gf_o|$ to that of the strongest scatterer in the structure was used as a basic damping factor for the refinement of the atom.

In the following applications to actual examples no contributions were included for D and its derivatives if $\left|\frac{F_c}{F_o}\right|$ was below 0·05. Regarding 'less than's', contributions have only been calculated in the case $|F_c|$ greater than $\sigma(F_o)$, substituting $\frac{1}{2}\sigma(F_o)$ for $|F_o|$.

This latter convention was also used for calculating R values:

$$R=\frac{\sum||F_o|-|F_c||}{\sum|F_o|}\,.$$

Applications

Some of the procedures discussed above have been successfully applied to the disordered crystal structures of trisallylchromium (Dietrich, 1969) and of bis-cyclooctatetraene-titanium (Dietrich & Soltwisch, 1969). Neither structure could be refined by least-squares methods, although in the case of the latter accurate diffractometer measurements were available.

In the mean time a more complete computer program has been prepared. Two applications will be discussed here in detail, one to a set of particularly good low-temperature neutron-diffractometer measurements from decaborane (Tippe & Hamilton, 1969) and one to a particularly bad set of visual film measurements from a twinned crystal of cyclododecatriene-1,5,9-nickel (Dietrich & Schmidt, 1965).

The low-temperature neutron-diffraction data have been chosen as an example because the series termination effect plays a much more important part than with X-ray measurements. So it should show whether the assumption about the influence of this effect on the peak shape of ϱ^* syntheses was sufficiently correct. Moreover, with space group $C2/a$ there are many systematic extinctions.

The Fourier refinement was started with a very bad parameter set ($R=0{\cdot}42$), given in columns 1 and 2 of Table 1, consisting of truncated positional parameters, uniform scattering lengths for all deuterium atoms and uniform and much too high isotropic B values of 3 Å^2 for all atoms. Although the scattering lengths of all deuterium atoms had to be refined, no low order reflexions were excluded from the calculations. As for the vibration parameter corrections equation (9) with $\left(\frac{G_c}{G_o}\right)^{2/5}$ set equal to 1 was used, but there was a serious interaction between $\Delta\beta$ and ΔG for some deuterium atoms. It was overcome by applying a damping factor of 0·7 to all ΔG's.

Columns 3 and 4 of Table 1 give the final parameter set ($R=0{\cdot}041$) which should be compared with that reached by least-squares methods, given in columns 5 and 6 ($R=0{\cdot}042$: Brill, Dietrich & Dierks, 1971). The maximum differences are about 2σ.

The second example (Fig. 2) was based on visual film measurements, which were rather inaccurate because the empirical intensity scales used did not fit the

Table 1. *Comparison of Fourier and least-squares refinement using low-temperature neutron-diffraction data of decaborane (Tippe & Hamilton, 1969)*

	Parameter	Input parameter set before Fourier refinement		Final parameter set after Fourier refinement		Final parameter set after least-squares refinement	
		Molecule 1	Molecule 2	Molecule 1	Molecule 2	Molecule 1	Molecule 2
B(1)	$b\times10^{12}$ cm	0·630	0·630	0·630	0·630	0·630	0·630
	x	0·0300	0·2800	0·0335	0·2844	0·0334 (1)	0·2843 (1)
	y	0·3300	0·4100	0·3316	0·4185	0·3315 (1)	0·4186 (1)
	z	0·0000	0·4900	−0·0000	0·4956	−0·0001 (3)	0·4955 (3)
	β_{11}	0·0037	0·0037	0·0014	0·0014	0·0015 (1)	0·0014 (1)
	β_{22}	0·0018	0·0018	0·0007	0·0007	0·0007 (0)	0·0007 (0)
	β_{33}	0·0237	0·0237	0·0099	0·0090	0·0103 (5)	0·0097 (5)
	β_{12}	0·0000	0·0000	−0·0000	0·0001	0·0000 (1)	0·0002 (1)
	β_{13}	−0·0000	−0·0000	0·0001	−0·0004	0·0002 (2)	−0·0004 (2)
	β_{23}	−0·0000	−0·0000	0·0005	0·0006	0·0005 (1)	0·0006 (1)
B(4)	$b\times10^{12}$ cm	0·630	0·630	0·630	0·630	0·630	0·630
	x	0·0900	0·3400	0·0979	0·3474	0·0980 (1)	0·3472 (1)
	y	0·1900	0·5500	0·1999	0·5508	0·2001 (1)	0·5505 (1)
	z	0·0000	0·4900	0·0007	0·4960	0·0006 (3)	0·4959 (3)
	β_{11}	0·0037	0·0037	0·0014	0·0013	0·0013 (1)	0·0014 (1)
	β_{22}	0·0018	0·0018	0·0007	0·0007	0·0008 (0)	0·0008 (0)
	β_{33}	0·0237	0·0237	0·0093	0·0091	0·0095 (5)	0·0093 (5)
	β_{12}	0·0000	0·0000	0·0003	−0·0001	0·0002 (1)	0·0000 (1)
	β_{13}	−0·0000	−0·0000	0·0001	−0·0003	0·0002 (2)	−0·0002 (2)
	β_{23}	−0·0000	−0·0000	−0·0005	−0·0005	−0·0004 (1)	−0·0005 (1)
H(1)	$b\times10^{12}$ cm	0·500	0·500	0·429	0·423	0·416 (7)	0·434 (7)
	x	0·0400	0·2900	0·0440	0·2958	0·0443 (3)	0·2959 (2)
	y	0·3800	0·3600	0·3890	0·3611	0·3892 (1)	0·3611 (1)
	z	0·0000	0·4900	−0·0066	0·4993	−0·0066 (7)	0·4994 (6)
	β_{11}	0·0037	0·0037	0·0033	0·0029	0·0031 (2)	0·0031 (2)
	β_{22}	0·0018	0·0018	0·0008	0·0009	0·0007 (1)	0·0008 (1)
	β_{33}	0·0237	0·0237	0·0249	0·0225	0·0234 (12)	0·0244 (12)
	β_{12}	0·0000	0·0000	−0·0001	0·0003	−0·0001 (1)	0·0002 (1)
	β_{13}	−0·0000	−0·0000	0·0005	0·0002	0·0007 (4)	−0·0002 (4)
	β_{23}	−0·0000	−0·0000	0·0006	0·0007	0·0007 (2)	0·0005 (2)
H(4)	$b\times10^{12}$ cm	0·500	0·500	0·415	0·440	0·427 (7)	0·430 (7)
	x	0·1500	0·4000	0·1578	0·4060	0·1575 (2)	0·4061 (3)
	y	0·1500	0·5900	0·1598	0·5913	0·1594 (2)	0·5917 (2)
	z	0·0000	0·5000	−0·0051	0·5020	−0·0053 (7)	0·5016 (7)
	β_{11}	0·0037	0·0037	0·0020	0·0023	0·0024 (2)	0·0024 (2)
	β_{22}	0·0018	0·0018	0·0013	0·0015	0·0012 (1)	0·0013 (1)
	β_{33}	0·0237	0·0237	0·0219	0·0229	0·0237 (12)	0·0221 (12)
	β_{12}	0·0000	0·0000	0·0007	−0·0004	0·0008 (1)	−0·0006 (1)
	β_{13}	−0·0000	−0·0000	0·0009	−0·0007	0·0008 (4)	−0·0001 (4)
	β_{23}	−0·0000	−0·0000	−0·0009	−0·0010	−0·0007 (2)	−0·0008 (2)

Table 1 (*cont.*)

	Param- eter	Input parameter set before Fourier refinement		Final parameter set after Fourier refinement		Final parameter set after least-squares refinement	
		Molecule 1	Molecule 2	Molecule 1	Molecule 2	Molecule 1	Molecule 2
B(2)	$b \times 10^{12}$ cm	0·630	0·630	0·630	0·630	0·630	0·630
	x	0·0900	0·3400	0·0993	0·3495	0·0993 (1)	0·3496 (1)
	y	0·2700	0·4700	0·2739	0·4768	0·2739 (1)	0·4768 (1)
	z	0·1700	0·3200	0·1721	0·3236	0·1726 (3)	0·3233 (3)
	β_{11}	0·0037	0·0037	0·0012	0·0011	0·0013 (1)	0·0012 (1)
	β_{22}	0·0018	0·0018	0·0008	0·0008	0·0008 (0)	0·0008 (0)
	β_{33}	0·0237	0·0237	0·0078	0·0079	0·0075 (5)	0·0080 (5)
	β_{12}	0·0000	0·0000	0·0000	0·0001	0·0000 (1)	0·0000 (1)
	β_{13}	−0·0000	−0·0000	−0·0005	0·0005	−0·0007 (2)	0·0003 (2)
	β_{23}	−0·0000	−0·0000	−0·0002	−0·0003	−0·0003 (1)	−0·0005 (1)
H(2)	$b \times 10^{12}$ cm	0·500	0·500	0·520	0·505	0·530 (7)	0·512 (7)
	x	0·1500	0·4000	0·1596	0·4094	0·1593 (2)	0·4095 (2)
	y	0·2800	0·4600	0·2886	0·4628	0·2883 (1)	0·4631 (1)
	z	0·3000	0·1800	0·3088	0·1866	0·3085 (5)	0·1867 (5)
	β_{11}	0·0037	0·0037	0·0022	0·0021	0·0025 (2)	0·0021 (2)
	β_{22}	0·0018	0·0018	0·0017	0·0016	0·0017 (1)	0·0016 (1)
	β_{33}	0·0237	0·0237	0·0147	0·0139	0·0165 (9)	0·0141 (9)
	β_{12}	0·0000	0·0000	−0·0003	0·0003	−0·0001 (1)	0·0002 (1)
	β_{13}	−0·0000	−0·0000	−0·0018	0·0022	−0·0018 (3)	0·0020 (2)
	β_{23}	−0·0000	−0·0000	−0·0010	−0·0010	−0·0007 (2)	−0·0007 (2)
B(3)	$b \times 10^{12}$ cm	0·630	0·630	0·630	0·630	0·630	0·630
	x	0·1100	0·3600	0·1188	0·3691	0·1187 (1)	0·3690 (1)
	y	0·2700	0·4700	0·2785	0·4724	0·2784 (1)	0·4724 (1)
	z	−0·1300	0·6200	−0·1307	0·6270	−0·1309 (3)	0·6273 (3)
	β_{11}	0·0037	0·0037	0·0015	0·0012	0·0015 (1)	0·0013 (1)
	β_{22}	0·0018	0·0018	0·0010	0·0010	0·0010 (0)	0·0010 (0)
	β_{33}	0·0237	0·0237	0·0086	0·0080	0·0083 (5)	0·0077 (5)
	β_{12}	0·0000	0·0000	−0·0001	0·0002	0·0000 (1)	0·0003 (1)
	β_{13}	−0·0000	−0·0000	0·0003	−0·0007	0·0001 (2)	−0·0006 (2)
	β_{23}	−0·0000	−0·0000	0·0003	−0·0000	0·0003 (1)	0·0002 (1)
H(3)	$b \times 10^{12}$ cm	0·500	0·500	0·408	0·404	0·404 (8)	0·414 (7)
	x	0·1800	0·4300	0·1860	0·4359	0·1858 (3)	0·4362 (2)
	y	0·2900	0·4500	0·2949	0·4561	0·2945 (2)	0·4565 (2)
	z	−0·2300	0·7300	−0·2368	0·7357	−0·2370 (7)	0·7355 (6)
	β_{11}	0·0037	0·0037	0·0023	0·0019	0·0021 (2)	0·0020 (2)
	β_{22}	0·0018	0·0018	0·0019	0·0018	0·0020 (1)	0·0019 (1)
	β_{33}	0·0237	0·0237	0·0196	0·0170	0·0196 (13)	0·0196 (12)
	β_{12}	0·0000	0·0000	−0·0004	0·0004	−0·0003 (1)	0·0004 (1)
	β_{13}	−0·0000	−0·0000	0·0020	−0·0022	0·0024 (4)	−0·0020 (3)
	β_{23}	−0·0000	−0·0000	0·0008	0·0006	0·0009 (3)	0·0007 (2)

various reflexion shapes on the films very well. Also it was not possible to grow single crystals (Wilke & Schmidt, 1964: unpublished work) and the Weissenberg photographs, *hk*0 to *hk*7, had been taken from a twinned crystal, which, moreover, decomposed gradually. The reciprocal lattices of the twins overlap systematically, as shown in Fig. 1, because the diagonal of the face a^*c^* of the reciprocal cell has just the same length as c^*. Generally the reflexion $(hkl)_{\rm I}$ of twin I coincides with $(-h-l,-k,l)_{\rm II}$ of twin II. The situation is improved, however, by the general systematic extinction of reflexions with $h+k=2n+1$ in the two possible space groups *Cc* and *C*2/*c*. Therefore the reflexions of the twins overlap only in the planes with l even, whereas for l odd the reflexions of twin I coincide with systematic extinctions of twin II. So, from measurements of the separated reflexions of twin II on the plane (*hk*1) the ratio of the twins could be derived. This was done, together with the general data reduction of the 7137 measurements on 74 data sets (films), by means of my data reduction program *DATKOR*, which yielded the layer lines *hk*0 to *hk*7 as 8 groups of reflexions on independent scales and a twin ratio of 1:0·18.

Starting with the nickel position derived in the two-dimensional treatment (Dietrich & Schmidt, 1965) of the structure, and ignoring the contributions of the weaker twin, a Fourier synthesis revealed all carbon positions. An attempt to refine them by least-squares methods, using space group *Cc* (all 12 carbon atoms in the asymmetric unit) and again ignoring the twin contributions, failed.

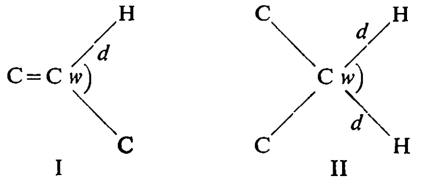
On the other hand the Fourier refinement program has been devised such that it accepts overlapped reflexions and also calculates weighted mean values of F_o's belonging to symmetry-related reflexions. Introducing an anisotropic temperature factor for the nickel atom and two isotropic B's, one of them shared

Table 1 (*cont.*)

	Parameter	Input parameter set before Fourier refinement		Final parameter set after Fourier refinement		Final parameter set after least-squares refinement	
		Molecule 1	Molecule 2	Molecule 1	Molecule 2	Molecule 1	Molecule 2
B(5)	$b \times 10^{12}$ cm	0·630	0·630	0·630	0·630	0·630	0·630
	x	0·0200	0·2600	0·0203	0·2696	0·0202 (1)	0·2696 (1)
	y	0·2000	0·5400	0·2087	0·5413	0·2087 (1)	0·5413 (1)
	z	0·2300	0·2500	0·2390	0·2569	0·2388 (3)	0·2568 (3)
	β_{11}	0·0037	0·0037	0·0015	0·0014	0·0013 (1)	0·0015 (1)
	β_{22}	0·0018	0·0018	0·0007	0·0007	0·0007 (0)	0·0007 (0)
	β_{33}	0·0237	0·0237	0·0068	0·0069	0·0072 (5)	0·0070 (5)
	β_{12}	0·0000	0·0000	0·0002	0·0000	0·0001 (1)	0·0001 (1)
	β_{13}	−0·0000	−0·0000	−0·0002	0·0000	−0·0001 (2)	0·0000 (2)
	β_{23}	−0·0000	−0·0000	0·0001	0·0003	0·0002 (1)	0·0003 (1)
H(5)	$b \times 10^{12}$ cm	0·500	0·500	0·560	0·557	0·558 (7)	0·541 (7)
	x	0·0300	0·2800	0·0366	0·2859	0·0365 (2)	0·2858 (2)
	y	0·1700	0·5700	0·1749	0·5755	0·1748 (1)	0·5755 (1)
	z	0·4000	0·0800	0·4066	0·0893	0·4064 (4)	0·0896 (4)
	β_{11}	0·0037	0·0037	0·0031	0·0032	0·0031 (2)	0·0029 (2)
	β_{22}	0·0018	0·0018	0·0013	0·0013	0·0013 (1)	0·0013 (1)
	β_{33}	0·0237	0·0237	0·0132	0·0143	0·0130 (8)	0·0127 (8)
	β_{12}	0·0000	0·0000	0·0003	−0·0001	0·0003 (1)	−0·0001 (1)
	β_{13}	−0·0000	−0·0000	−0·0003	0·0004	−0·0007 (2)	0·0006 (2)
	β_{23}	−0·0000	−0·0000	0·0014	0·0019	0·0012 (1)	0·0016 (2)
H(6)	$b \times 10^{12}$ cm	0·500	0·500	0·389	0·385	0·373 (7)	0·369 (7)
	x	0·0400	0·2900	0·0451	0·2963	0·0444 (3)	0·2960 (3)
	y	0·3100	0·4300	0·3112	0·4387	0·3108 (2)	0·4385 (2)
	z	−0·2200	0·7100	−0·2228	0·7173	−0·2223 (6)	0·7172 (6)
	β_{11}	0·0037	0·0037	0·0024	0·0026	0·0019 (2)	0·0022 (2)
	β_{22}	0·0018	0·0018	0·0016	0·0014	0·0016 (1)	0·0014 (1)
	β_{33}	0·0237	0·0237	0·0118	0·0114	0·0113 (11)	0·0107 (11)
	β_{12}	0·0000	0·0000	−0·0000	0·0002	0·0000 (1)	0·0001 (1)
	β_{13}	−0·0000	−0·0000	0·0001	−0·0000	0·0000 (3)	0·0000 (3)
	β_{23}	−0·0000	−0·0000	0·0003	0·0008	0·0006 (2)	0·0006 (2)
H(7)	$b \times 10^{12}$ cm	0·500	0·500	0·389	0·378	0·385 (7)	0·365 (7)
	x	0·0800	0·3300	0·0901	0·3379	0·0897 (3)	0·3380 (3)
	y	0·2200	0·5200	0·2212	0·5294	0·2208 (2)	0·5294 (2)
	z	−0·2200	0·7100	−0·2219	0·7187	−0·2217 (6)	0·7184 (6)
	β_{11}	0·0037	0·0037	0·0026	0·0025	0·0026 (2)	0·0023 (2)
	β_{22}	0·0018	0·0018	0·0015	0·0014	0·0015 (1)	0·0014 (1)
	β_{33}	0·0237	0·0237	0·0107	0·0106	0·0110 (11)	0·0096 (11)
	β_{12}	0·0000	0·0000	−0·0000	0·0002	0·0000 (1)	0·0003 (1)
	β_{13}	−0·0000	−0·0000	0·0005	−0·0001	0·0004 (3)	−0·0007 (3)
	β_{23}	−0·0000	−0·0000	−0·0009	−0·0006	−0·0006 (2)	−0·0006 (2)

by all sp^2 carbon atoms and the other one shared by the sp^3 carbons, the structure refined to $R=0{\cdot}11$, both using space group *Cc* and *C*2/*c*. In both cases the deviations of chemically equivalent bond lengths and angles from their mean values became smaller, but were clearly better with *C*2/*c*, although the mean values themselves were identical for both parameter sets. Therefore the refinement was continued with *C*2/*c* only, introducing hydrogen atoms and a variable occupancy factor G for the nickel atom (with ΔG damped again by 0·7). The variation of G_{Ni} was suggested by a large hole of $-0{\cdot}72$ e.Å^{-3} at the nickel position in the difference synthesis. It also agrees with the fact that crystals of the free cyclododeca-1,5,9-triene (Allegra & Bassi, 1962) are isomorphous with the Ni complex (Dietrich & Schmidt, 1965) and any intermediates which have been found (Wilke *et al.*, 1964: unpublished). Moreover, the decomposition of the crystal seemed to be due mainly to loss of nickel atoms, as the wall of the glass capillary in which the crystal had been sealed was coated by a metal film.

Although for the strongest reflexions calculated intensities were much higher than observed, no reflexions were excluded from the refinement. The occupancy factor G of the Ni atom dropped to 0·92 and R to 0·097. In this last phase of the refinement the hydrogen atoms were treated in two groups, I and II:



I II

Three parameters of each group were varied: the distance d, the angle W and an additive term ΔB, used for the evaluation of a vibration parameter B_{H} of the hydrogen atoms from that of the corresponding carbon atom,

$$B_{\text{H}}=B_{\text{C}}+\Delta B\,.$$

Table 2 shows the final parameters of the structure and Fig. 2 gives bond lengths and angles. They are quite normal for a complex involving strong π-complex bonds [averaged distance Ni–C(sp^2) 2·03 Å]. The latter is not in agreement with speculations based on an earlier two-dimensional study (Dietrich & Schmidt, 1965) which had suggested 2·11 Å for the averaged distance. The assumption that the nickel atom occupies the centre of the ring is confirmed, however, by the present work.

Since about 8 % of the nickel atoms are missing, one cannot expect very accurate parameters for the organic part of the molecule, because in the free cyclododecatriene the double bonds are, of course, shorter and also the bond angles and the conformation of the ring may be somewhat different. Moreover, it must be remembered that the crystal was decaying while the photographs were being taken, so that the latter probably refer to varying compositions of the crystal.

These are possibly two of the reasons for the fact that an attempt to refine the structure with individual B values for all carbon atoms gave rather unrealistic results. Also, presumably the group parameter refinement applied to the hydrogen atoms has no physical significance. An attempt to introduce anisotropic vibration parameters for the carbon atoms had failed completely because of the interaction between the scale factors of the eight layer lines with the thermal parameters B_{33}; this could, however, have been expected.

Bearing in mind the various systematic errors in the data, the structure should be a good example for representation by partial F_o Fourier sections ϱ_o^* to show the fit of model and data in direct space. This is given in Fig. 3.

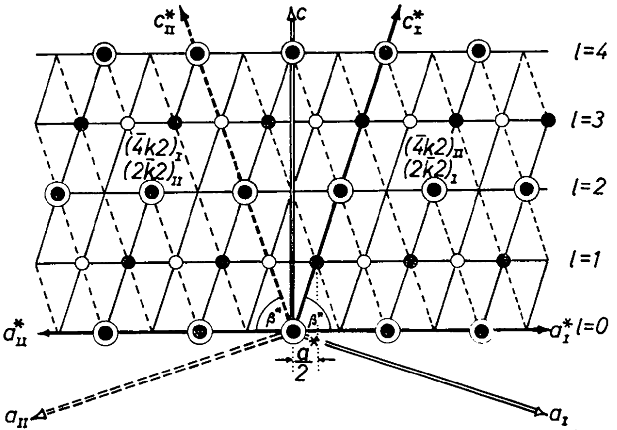


Fig. 1. Coinciding reciprocal lattices of the twins I and II in a crystal of all-*trans*-cyclododeca-1,5,9-triene-nickel.

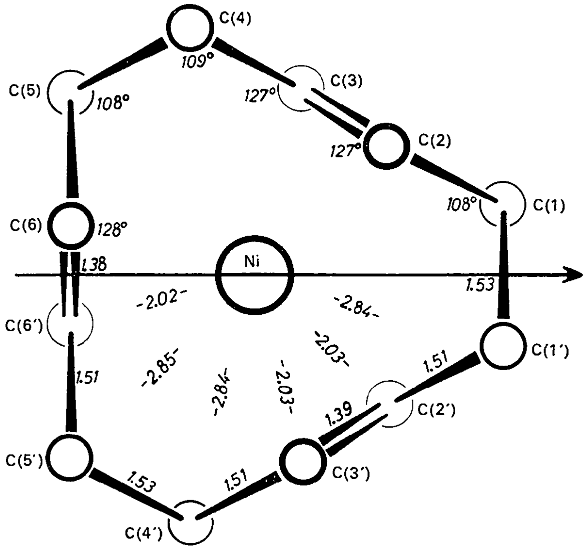


Fig. 2. Intramolecular distances and angles in all-*trans*-cyclododeca-1,5,9-triene-nickel.

Table 2. *Structure parameters for all-trans-cyclododeca*-1,5,9-*triene-nickel, space group* $C2/c$, $R=0·097$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	G
Ni	3·04	2·81	2·79	0·00	1·88	0·00	0·92

	x	y	z	B (Å^2)	ΔB	d (Å)	W (°)
Ni	0·5000	0·6165	0·2500	($\bar{B}$=2·66)			
C(1)	0·4451	0·9397	0·2059	3·56			
C(2)	0·4022	0·7897	0·2478	3·26			
C(3)	0·3560	0·6683	0·1481	3·26			
C(4)	0·3007	0·5311	0·1854	3·56			
C(5)	0·3532	0·3774	0·1729	3·56			
C(6)	0·4585	0·3918	0·2729	3·26			
H(1)	0·436	0·938	0·088	5·7	2·2	1·03	115
H(11)	0·414	1·035	0·244	5·7	2·2	1·03	115
H(2)	0·408	0·776	0·367	4·9	1·7	1·06	116
H(3)	0·360	0·672	0·033	4·9	1·7	1·06	116
H(4)	0·232	0·528	0·103	5·7	2·2	1·03	115
H(44)	0·301	0·543	0·299	5·7	2·2	1·03	115
H(5)	0·351	0·364	0·059	5·7	2·2	1·03	115
H(55)	0·321	0·287	0·217	5·7	2·2	1·03	115
H(6)	0·471	0·403	0·395	4·9	1·7	1·06	116

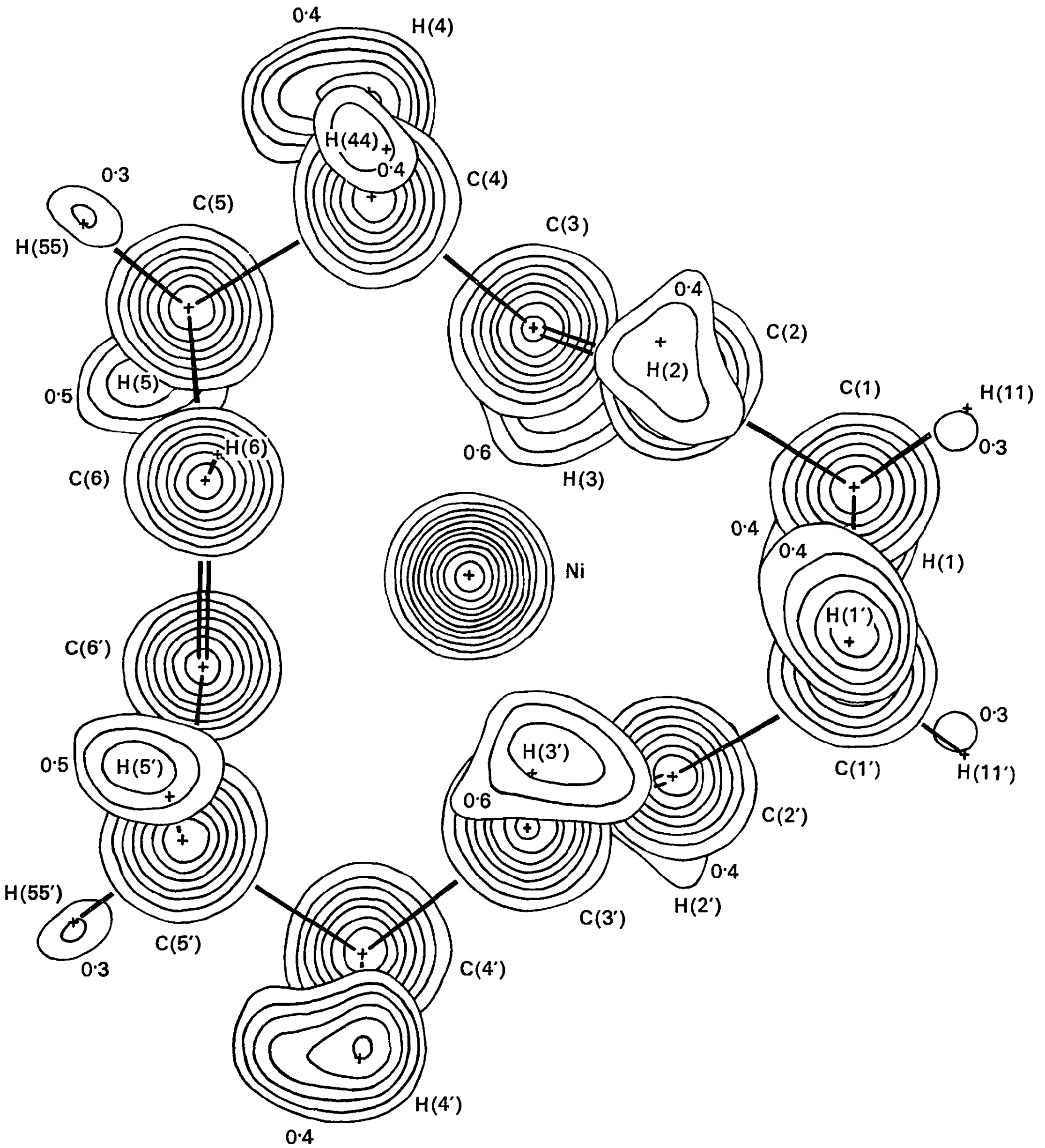


Fig. 3. ϱ_0^* sections parallel to xy through the atoms. Outer contours and contour intervals (in parentheses) are 5(5) for Ni, 1(1) for C, and (0·1) e.Å^{-3} for H, the first contour being labelled in the figure.

The model obtained is, again with respect to the data, not too bad, since the bond lengths and angles (Fig. 2) are quite reasonable, as are the vibration parameters (Table 2). This again suggests that the Fourier refinement is rather insensitive to systematic errors. On the other hand, with accurate data practically the same results were obtained as by least-squares methods. Therefore Fourier refinement might also be useful for structures with many variable parameters, when full-matrix or large block-diagonal least-squares procedures would require too much machine storage or computing time.

All olefin complexes of transition metals cited in this paper were synthesized by Professor G. Wilke and coworkers, whom I thank for the crystals used. For lists and punched cards of the low-temperature neutron-diffraction data of decaborane I am indebted to Professor W. C. Hamilton and Dr A. Tippe. Thanks for valuable discussions are due to Dr C. Scheringer, Dr D. Weick, Professor K. Weber and Dr J. Gassmann. For the film measurements from the cyclododecatriene complex I thank Mrs A. Dreissig and Mr H. Schmidt. I thank Dr Hertweck for allowing me to use the IBM 360 machine of the Institute für Plasmaphysik at Garching. For financial support I am indebted to Professors R. Brill and H. Gerischer.

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The Crystal and Molecular Structure of a Tetracyclic Diketone, $C_{13}O_2H_{16}$*

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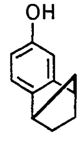
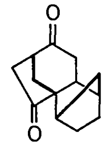
Tetracyclic diketone $C_{13}O_2H_{16}$, m.p. 124°C, was prepared by K. Wiesner, A. Deljac and T.Y.R. Tsai in the process of developing a new stereospecific method for the synthesis of bridged terpenoids. The crystals belong to the space group $C2/c$ with eight molecules in a unit cell of dimensions: $a = 16{\cdot}214$ (4), $b = 6{\cdot}194$ (4), $c = 24{\cdot}198$ (4) Å and $\beta = 119{\cdot}06$ (3)°. The data, consisting of 1563 observed reflexions, were collected with a Picker automatic and a General Electric XRD-5 manual diffractometer. The structure was solved by the symbolic addition procedure for phase determination for centrosymmetric space groups, and refined by block-diagonal least-squares cycles to a final R value of 0·042. The molecules are held by the dipole attraction between carbonyl groups.

Introduction

New stereospecific methods for the conversion of phenol (I) to two tetracyclic diketones (II and III) were developed by K. Wiesner and his collaborators. These methods are expected to be useful, not only in the synthesis of songorine (IV), but also in the synthesis of many other bridged terpenoids.



I



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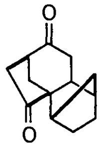
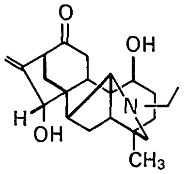


III



IV

While the stereochemistry of the cyclization of (I) leading to the formation of one or the other tetracyclic diketone was well controlled, it was not known which one corresponded to the structural formula II. The assignment of stereochemistry by a chemical method would be difficult; moreover, a direct comparison with the degradation product of songorine was not possible because of a very limited supply of this alkaloid. In view of the considerable synthetic value of Wiesner's method, an X-ray analysis of one of the diketones was warranted.

The crystals of both tetracyclic diketones were obtained from K. Wiesner. The compound of m.p. 124°C was chosen and was found to have the structure II and its enantiomer. By analogy, the structure of the second diketone, of m.p. 108–109°C, which was characterized by infrared, n.m.r. and mass spectrometry, can be assumed to be III.

The syntheses of the diketones and the result of this investigation have been reported by Wiesner, Deljac, Tsai & Przybylska (1970).

Experimental

Tetracyclic diketone, $C_{13}O_2H_{16}$, m.p. 124°C, F.W. = 204·26.

Monoclinic, $a = 16{\cdot}214$ (4), $b = 6{\cdot}194$ (4), $c = 24{\cdot}198$ (4) Å, $\beta = 119{\cdot}06$ (3)°.

$V = 2124{\cdot}3$ Å^3, $Z = 8$.

$D_m = 1{\cdot}26$ g.cm^{-3}, by flotation in a mixture of toluene and carbon tetrachloride;

$D_x = 1{\cdot}28$ g.cm^{-3}. $F(000) = 880$.

Systematic absences from precession photographs: hkl, when $h+k$ is odd and $h0l$, when l is odd. Space group $C2/c$. $\mu(\mathrm{Cu}) = 6{\cdot}8$ cm^{-1}.

The crystals were recrystallized from ethyl acetate. They were elongated along the b axis with (001) faces

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