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Crystal data for some dicyclopentadienyldinickel alkyne compounds.

By O. S. Mills and B. W. Shaw, *Department of Chemistry, University of Manchester, Manchester* 13, *England*

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It has been shown (Tilney-Bassett & Mills, 1959; Tilney-Bassett, 1961) that dicyclopentadienyldinickel dicarbonyl reacts with acetylenes in a manner similar to dicobalt octacarbonyl (Sternberg, Greenfield, Friedel, Wotiz, Markby & Wender, 1954; Greenberg, Sternberg, Friedel, Wotiz, Markby & Wender, 1956). It was suggested that the molecular structures of these nickel compounds would be comparable to the corresponding cobalt derivatives, the structure of one of which has been determined (Sly, 1959).

In the course of our verification of these proposals we have determined the unit-cell dimensions of six derivatives and these are given in Table 1. Measurements were made on precession photographs taken with either molybdenum $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) or with cobalt $K\alpha$ radiation ($\lambda = 1{\cdot}7902$ Å). Densities were determined by suspension in aqueous solutions of potassium iodide. The determination of the structure of derivative A has been completed. No further work on the remaining compounds is contemplated.

References

Greenfield, H., Sternberg, H. W., Friedel, R. A., Wotiz, J., Markby, R. & Wender, I. (1956). *J. Amer. Chem. Soc.* **78**, 120.

Sly, W. G. (1959). *J. Amer. Chem. Soc.* **81**, 18.

Sternberg, H. W., Greenfield, H., Friedel, R. A., Wotiz, J., Markby, R. & Wender, I. (1954). *J. Amer. Chem. Soc.* **76**, 1457.

Tilney-Bassett, J. F. (1961). *J. Chem. Soc.* p. 577.

Tilney-Bassett, J. F. & Mills, O. S. (1959). *J. Amer. Chem. Soc.* **81**, 4757.

Table 1. *Crystal data for dicyclopentadienyldinickel alkynes*

Derivative	*A*	*B*	*C*	*D*	*E*	*F*
Space group	$Pna2_1$	$P2_1/n$	$P2_1$ or $P2_1/m$	$P2_12_12_1$	$P1$ or $P\bar{1}$	$P1$ or $P\bar{1}$
Unit cell (Å)						
a	17·73(5)	23·87(6)	6·15(3)	17·60(5)	10·90(4)	5·73( )
b	9·49(3)	5·75(3)	12·37(4)	20·17(5)	11·57(4)	10·71( )
c	11·62(4)	10·63(4)	8·75(3)	8·67(3)	18·99(4)	13·08( )
α					118° 47′(5)	101° 45′
β		92° 36′(5)	100° 36′(5)		91° 4′(5)	108° 57′
γ					90° 30′(5)	90° 2′
D_m (g.cm^{-3})	1·45(2)	1·50(2)	1·52(2)	1·50(2)	1·41(2)	1·57(2)
D_x (g.cm^{-3})	1·45(1)	1·50(1)	1·53(1)	1·50(1)	1·42(1)	1·57(1)
Z	4	4	2	4	2	2
Radiation used	Cobalt	Molybdenum	Cobalt	Molybdenum	Molybdenum	Molybdenum

A. $Cy_2Ni_2C_6H_5C_2C_6H_5$
B. $Cy_2Ni_2HC_2n\text{-}C_4H_9$
C. $Cy_2Ni_2CH_3C_2CH_3$
D. $Cy_2Ni_2C_6H_5C_2C_2C_6H_5Ni_2Cy_2$
E. $Cy_2Ni_2C_6H_5C_2C_2C_6H_5$
F. $Cy_2Ni_2C_6H_5C_2H$

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Bond lengths and thermal vibrations in orthorhombic sulfur.

By Aimery Caron and Jerry Donohue
Department of Chemistry, University of Southern California, Los Angeles 7, *California, U.S.A.*

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Abrahams (1961) has recently re-refined the structure of orthorhombic sulfur, using an improved form factor curve (Dawson, 1960*a*, *b*) and scale factors differing by 15 to 24% from the one used in his earlier work (Abrahams, 1955). In this note, Abrahams gave two widely differing sets of r.m.s. thermal displacements. One set, labelled 1960*A*, was obtained by assigning unit weights to observed reflections and weights of 0·1 to the unobserved reflections for which the F_o were set at $\frac{1}{2}F_{\min}$. In obtaining the second set, labelled 1960*C*, the Hughes (1941) weighting scheme was used, with $4F_{\min} = 100$ and weights of 0·05 for the unobserved reflections. Individual positional and thermal parameters and their standard errors were not given; values of R were not mentioned. Abrahams suggested that there was correlation among the thermal parameters and thus implied that the thermal displacement values which he presented should not be discussed from a physical standpoint.

We feel, however, that the 1960*A* weighting scheme is indefensible, a conclusion supported by common sense, by the higher standard deviations for the 1960*A* results, and by Abrahams's (1955) comment on his data to the effect that 'The standard deviation in the [observed] structure factor was then found to be, approximately, a constant percentage of the structure factor, with $\sigma(F_i) \simeq 0\cdot07|F_i|$. This relation is violated most for $|F_i| < 100$.' We also believe that the introduction into the refinement of unobserved F's at half value may create some problems, particularly in the present case where almost 40% of the reflections were unobserved. We therefore decided to undertake additional refinement, based on the Hughes weighting scheme, in order to obtain new values for the positional and thermal parameters. This was done with the Dawson (1960*b*) form factor curve and the Palenik (1962) full-matrix program. After four cycles, R dropped from 26·5 to 12·4%. An examination of the F_o's at this point revealed that some of them were so discrepant as to warrant rejection (see Table 1). Such gross discrepancies as presented in Table 1 could result from errors in, *inter alia*, indexing or reduction of raw data, from the Renninger effect, or from just plain mistakes. It is interesting that nearly all of these F's were also outstandingly discrepant in the former work (Abrahams, 1955, Table 9). Because these discrepancies were apparently not systematic, these F's were assigned weight zero and the refinement was continued on the remaining 651 $F_{\rm obs}$. The largest of these F's obviously did suffer from some systematic error, such as extinction or some other effect with a similar result, as may be seen in Fig. 1. Correction for this 'extinction' effect was made with the following expression: $F^2_{\rm corr} = F^2_{\rm uncorr}/(1-2gF^2_{\rm uncorr})$, where a value for $2g$ of $1\cdot6\times10^{-6}$ was obtained by trial and error. The $F_{\rm uncorr}$ were on a scale of 0·7625 relative to the published values. If the systematic error evident in Fig. 1 is truly due to extinction, the correction of the $F^2_{\rm obs}$ rather than the $I_{\rm obs}$ is obviously incorrect; we feel, however, that since the $I_{\rm obs}$ are not available, it is far better to make the incomplete correction to the F^2, rather than to make no correction at all. Refinement was then resumed, and R dropped to a value of 10·5%. The shifts in the last cycle were all less than 10^{-6}. The resulting parameters and their standard errors are shown in Table 2.

Table 1. *Discrepant* $F_{\rm obs}$

hkl	F_o	F_c	*hkl*	F_o	F_c
0,0,36	20	2	8,4,10	20	6
5,1,23	81	6	14,4,6	27	3
7,1,23	38	2	3,5,21	23	0
1,3,31	30	11	5,5,29	23	2
13,3,9	20	3	6,6,26	27	4
4,4,24	29	5	1,7,23	27	6
4,4,30	27	7	9,7,9	21	3
4,4,34	56	16	8,8,18	22	4
6,4,28	25	7	6,14,0	21	3

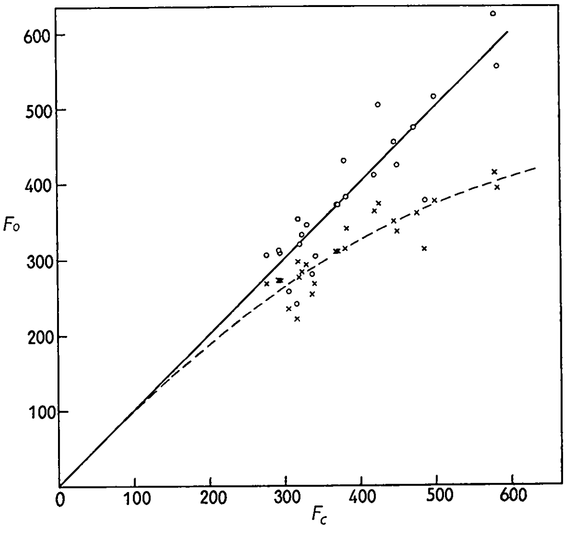

Fig. 1. Agreement between F_o and F_c for the 24 strongest reflections: × uncorrected F_o, ○ F_o corrected for 'extinction' (see text).

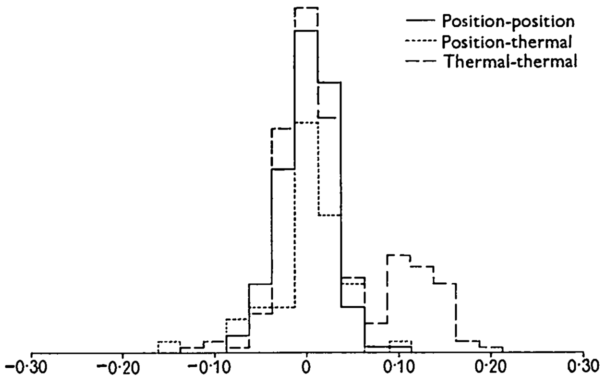

Fig. 2. Histogram of inter-atomic correlations.

Table 2. *Parameters obtained from the corrected* $F_{\rm obs}$

All values have been multiplied by 10^4. Values in parentheses include the libration corrections

	S(1)			S(2)			S(3)			S(4)		
			σ			σ			σ			σ
x	8563	(8563)	3	7845	(7842)	3	7076	(7066)	3	7860	(7855)	3
y	9529	(9535)	3	10305	(10315)	2	9799	(9805)	3	9078	(9080)	3
z	9516	(9511)	1	10762	(10763)	1	10039	(10037)	1	11296	(11300)	1
B_{11}	122		4	115		4	93		3	73		3
B_{22}	57		2	55		2	70		2	87		3
B_{33}	13		<1	16		<1	15		<1	13		<1
B_{12}	5		4	2		4	34		4	-6		4
B_{13}	12		2	6		2	-8		2	10		2
B_{23}	11		2	-11		2	1		2	4		2

Table 3. *Average intra-atomic correlation coefficients*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	G
x	1·0	0·02	0·04	−0·02	< 0·01	0·02	−0·02	−0·01	> −0·01	0·01
y		1·0	< 0·01	0·01	0·01	−0·02	< 0·01	−0·01	−0·01	0·01
z			1·0	> −0·01	< 0·01	−0·04	0·01	< 0·01	−0·02	−0·02
B_{11}				1·0	−0·09	−0·06	0·04	0·03	< 0·01	0·35
B_{22}					1·0	−0·06	0·05	< 0·01	0·02	0·33
B_{33}						1·0	< 0·01	0·04	0·02	0·35
B_{12}							1·0	< 0·01	0·03	0·02
B_{13}								1·0	0·04	> −0·01
B_{23}									1·0	0·01
G										1·0

Table 4. *Maximum intra-atomic correlation coefficients*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	G
x	1·0	0·10	0·09	−0·05	−0·05	0·04	0·04	−0·05	0·02	0·06
y		1·0	−0·11	−0·04	0·07	−0·04	−0·04	−0·02	0·03	−0·04
z			1·0	−0·04	0·04	−0·19	0·02	−0·01	−0·08	−0·04
B_{11}				1·0	−0·10	−0·09	0·08	0·09	0·01	0·39
B_{22}					1·0	−0·09	0·16	0·02	0·12	0·39
B_{33}						1·0	0·13	0·10	−0·14	0·37
B_{12}							1·0	0·08	0·07	0·04
B_{13}								1·0	0·10	−0·01
B_{23}									1·0	0·05
G										1·0

Since Abrahams (1961) suggested that there is some 'indeterminacy' due to correlation effects between parameters, the correlation coefficient matrix was calculated (Gantzel, Sparks & Trueblood, 1962) with the results as shown in Tables 3 and 4 and Fig. 2. All the coefficients are satisfactorily low except those having to do with the correlation of the B_{ii} with the scale factor. This effect is not unexpected and is known to become more accentuated as the number of atoms in the asymmetric unit decreases. However, these coefficients are not so large as to render the temperature factors meaningless from a physical standpoint or worthless for a rigid-body analysis since they will affect the molecular translational parameters rather than the librational ones and, thus, would not bias the bond lengths or angles.

The thermal parameters were used to calculate (Coulter, Gantzel & Trueblood, 1962) the r.m.s. displacements and direction cosines of the principal axes of the four vibration ellipsoids (Table 5). A comparison of the displacements with the 1960*C* values of Abrahams shows that they are of the same order of magnitude but that the former are generally larger. Abrahams did not publish values for the direction cosines, so we shall not make further detailed comparisons of our thermal parameters with his.

Table 5. *Ellipsoids of vibration*

	$\|\overline{r^2}\|^{1/2}$, A	q_{ia}	q_{ib}	q_{ic}
S(1)	0·265	−0·9332	−0·1929	−0·3033
	0·228	−0·3126	0·8522	0·4195
	0·183	−0·1776	−0·4863	0·8556
S(2)	0·255	0·9516	−0·1037	0·2892
	0·236	0·2842	0·6549	−0·7003
	0·196	0·1168	−0·7486	−0·6527
S(3)	0·260	0·6062	0·7863	−0·1198
	0·221	0·4615	−0·4704	−0·7522
	0·197	0·6478	−0·4007	0·6479
S(4)	0·270	0·0458	−0·9962	−0·0744
	0·216	0·7227	−0·0184	0·6910
	0·181	0·6897	0·0854	−0·7191

A rigid-body analysis (Cruickshank, 1956) was then made. The translational and librational amplitudes and the direction cosines of the principal axes of the **T** and **ω** tensors are given in Table 6. Since the S_8 molecule is located on a twofold axis parallel to c, one principal axis of both **ω** and **T** is restricted to that direction. It should be noted that the remaining **ω** and **T** axes differ in direction from the other two molecular axes by only about 8·9° and 2·7° respectively. Furthermore, the two largest and nearly equal librational amplitudes are associated with the two lowest and equivalent moments of inertia. This qualitative reasonableness of the translational and vibrational motions accordingly lends support to the assumption that the molecule may in fact be treated as a rigid body and attests to the physical significance of the thermal parameters. In the following note Abrahams (1965) refers to an unpublished infrared study in which the internal vibrations of the molecule were derived. The displacements of 0·049 Å, 3·26° and 4·93° quoted by him for r, θ and φ, respectively, correspond to mean square displacements in the position of an atom of 0·0006, 0·0012 and 0·0030 Å^2 respectively. The values of **ω** (5·6°, 5·2° and 2·5°) correspond to mean square displacements of 0·0098, 0·0086 and 0·0106 Å^2. It thus appears that the internal vibrations are, as expected, virtually negligible compared with the thermal vibrations and well within their assigned standard errors.

The positional parameters were then transformed to the orthogonal system of principal axes of **ω**, and each coordinate was corrected as follows: $x_{\text{corr}} = x_{\text{uncorr}}$ (sec ω_y + sec $\omega_z - 1$), where ω_y and ω_z are the r.m.s. angles of libration around the redefined y and z axes. The corrected coordinates reconverted to the system of the crystal axes are given in Table 2.

From these new coordinates, bond lengths and angles were calculated. These values are presented in Table 7, together with the present uncorrected values and those

Table 6. *Translational and librational parameters*

i	$\|\overline{T^2}\|^{1/2}$, *A*	$\|\overline{\omega^2}\|^{1/2}$, deg.	q_{ia}	q_{ib}	q_{ic}
1		5·58 ± 0·39	0	0	1
2		5·16 ± 0·33	−0·7375	0·6753	0
3		2·54 ± 0·82	−0·6753	−0·7375	0
1	0·189 ± 0·006		0	0	1
2	0·213 ± 0·014		−0·6620	0·7495	0
3	0·105 ± 0·026		−0·7495	−0·6620	0
1	(molecular axes)		0	0	1
2			−0·6237	0·7816	0
3			−0·7816	−0·6237	0

of Cooper, Bond & Abrahams (1961) set 1960*C*. The standard deviations for the corrected bond lengths include the contribution from the standard deviations, $\sigma_\omega(r)$, of the rigid-body least-squares fit.

Table 7. *Bond lengths* (Å) *and bond angles* (°)

Standard errors × 10³ in Å and × 10 in degrees in parentheses

	Abrahams 1960*C* (1961)	This work, uncorrected	This work, corrected
S(1)–S(3)	2·045 (5)	2·045 (5)	2·058 (5)
S(3)–S(2)	2·051 (4)	2·050 (5)	2·062 (5)
S(2)–S(4)	2·048 (5)	2·050 (5)	2·063 (5)
S(1)–S(1′)	2·043 (7)	2·042 (6)	2·058 (7)
S(4)–S(4′)	2·050 (7)	2·045 (7)	2·057 (7)
Mean S–S	2·048 (2)	2·047 (3)	2·060 (3)
S(1)–S(3)–S(2)	107·2	107·2 (2)	107·1 (2)
S(3)–S(2)–S(4)	108·0	108·0 (2)	107·9 (2)
S(2)–S(4)–S(4′)	109·0	109·0 (2)	108·9 (2)
S(1′)–S(1)–S(3)	108·2	108·2 (2)	108·1 (2)
Mean S–S–S	107·9 (1)	108·1 (1)	108·0 (1)

In order to insure that the $\sigma_\omega(r)$ are meaningful, standard deviations were computed for the same quantities using only the standard deviations of B_{ij} according to the expression:

$$\sigma_B(r)^2 = \Sigma_m \Sigma_{ij} \sigma^2_{(B_{ij})m} [\partial\Delta(r)/\partial(B_{ij})_m]^2 ,$$

where $\sigma_B(r)$ is the standard deviation for the rth bond length correction, $\Delta(r)$ is the rth bond length correction, $\sigma(B_{ij})_{\rm m}$ is the standard deviation of the B_{ij} of the mth atom. The change of the rth bond length correction with respect to the B_{ij} of the mth atom, $\partial\Delta(r)/\partial(B_{ij})_{\rm m}$, was computed numerically using increments of B_{ij} of the same order of magnitude as its standard deviation, namely 2×10^{-4}. The resulting values of $\sigma_B(r)$ are given in Table 8, together with those of $\sigma_\omega(r)$. In addition, since the introduction of the extinction correction seemed to have generally raised the B_{ij} values, a new set of bond length corrections was calculated with B_{ij} values obtained from a refinement with uncorrected data. The deviations of this set of bond length corrections from the previous set are negligible and also appear in Table 8. On the average, $\sigma_\omega(r)$ is 1·5 times as large as $\sigma_B(r)$; thus, the standard deviations derived from the rigid-body analysis appear meaningful and reflect, to some extent, the uncertainties in the B_{ij}.

Table 8. *Standard deviations* (Å) *for the libration corrections of the bond lengths*

All values have been multiplied by 10⁴

Bond	Libration correction	$\sigma_B(r)$	$\sigma_\omega(r)$	Extinction Δ
S(1)–S(3)	121	10	12	−1
S(3)–S(2)	123	8	13	−1
S(2)–S(4)	132	9	13	0
S(1)–S(1′)	139	10	14	1
S(4)–S(4′)	123	9	16	−1

In conclusion, the thermal parameters seem to have physical significance and indications are that the accuracy of the data warrants the application of the libration corrections to the bond lengths. It is noteworthy that the corrected bond lengths are significantly longer than the uncorrected values, and, until better experimental data become available, yield the best average value of 2·060 ± 0·003 Å for the S–S bond length and 108·0 ± 0·1° for the S–S–S bond angle in the S_8 molecule. The average libration correction found here of +0·013 Å is but +0·005 Å larger than the maximum correction of 0·008 Å mentioned by Abrahams (1955) in his first paper as possible for this effect.

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References

Abrahams, S. C. (1955). *Acta Cryst.* **8**, 661.

Abrahams, S. C. (1961). *Acta Cryst.* **14**, 311.

Abrahams, S. C. (1965). *Acta Cryst.* **18**, 566.

Cooper, A. S., Bond, W. L. & Abrahams, S. C. (1961). *Acta Cryst.* **14**, 1008.

Coulter, C. L., Gantzel, P. K. & Trueblood, K. N. (1962). I.U. Cr. *World List of Crystallographic Computer Programs*, p. 35, No. 232.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Dawson, B. (1960*a*). *Acta Cryst.* **13**, 409.

Dawson, B. (1960*b*). *Acta Cryst.* **13**, 403.

Gantzel, P. K., Sparks, R. A. & Trueblood, K. N. (1962). I.U. Cr. *World List of Crystallographic Computer Programs*, p. 34, No. 384.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

Palenik, G. (1962). I.U. Cr. *World List of Crystallographic Computer Programs*, p. 34, No. 308.