reflexions were estimated visually and corrected for Lorentz and polarization factors. No absorption corrections were applied.

The least-square refinement was started with the atomic parameters given by Stackelberg & Paulus (1935) for Zn_3P_2. The calculations were performed on an Elliott 803 computer using a program (written by one of us, K.Ł.) with the diagonal approximation and isotropic temperature factors. The reflexions 040, 224 and 440, probably affected by extinction, were omitted. Atomic scattering factors for the neutral atoms Cd and As were taken from *International Tables for X-ray Crystallography* (1962) and corrected for anomalous scattering. After 10 cycles of refinement the R index (calculated for observed reflexions only) dropped from 0·24 to 0·138. Atomic parameters are given in Table 1, and the comparison of observed and calculated structure factors in Table 2. Interatomic distances, presented in Table 3, agree well with those given by Steigmann & Goodyear (1968) for Cd_3As_2, which according to our notation should be named α-Cd_3As_2.

A full discussion of phase transitions in the single composition Cd_3As_2 system will be possible after a determination of the crystal structure of α' Cd_3As_2.

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Acta Cryst. (1969). B**25**, 990

Zur Kristallographie der heterosubstituierten Fulvene.

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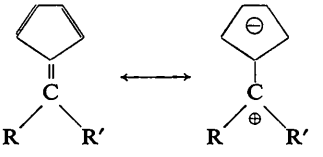
The lattice parameters and the possible space groups for 12 different fulvenes are given; for three of them, structure determination has been started.

Heterosubstituierte Fulvene mit elektronenspendenden Substituenten R und R′ (z. B. R = R′ = Dialkylamino-, Alkylarylamino-, Alkoxy oder Alkylmercapto) haben im Laufe der letzten Jahre zunehmendes Interesse gefunden.



(*A*) (*B*)

Im Vergleich mit den klassischen 6,6-Dialkyl- und 6,6-Diarylfulvenen (Bergmann, 1968) ist bei ihnen der Anteil der dipolaren Grenzform *B* am Grundzustand erheblich verstärkt. Spektroskopische Daten (NMR, IR und UV) sowie Dipolmomente erlauben die qualitative Aussage, dass der Bindungszustand der heterosubstituierten Fulvene eine Zwischenstellung einnimmt: Er lässt sich weder als typisch gekreuzt konjugiertes Doppelbindungssystem im Sinne der mesomeren Grenzform *A* noch als typisch nicht-benzoider aromatischer Carbocyclus im Sinne der mesomeren Grenzform *B* beschreiben.

Um bessere Vorstellungen über die Bindungsverhältnisse zu gewinnen, scheint es wünschenswert, möglichst genaue Winkel und Abstände zwischen den Atomen bei einigen Vertretern der heterosubstituierten Fulvene mit Hilfe einer Röntgenstrukturanalyse zu bestimmen, zumal ausser der Strukturuntersuchung am klassischen 6,6-Dimethylfulven (Norman & Post, 1961) bisher keine röntgenographischen Methoden angewendet worden sind.

Zur Vorbereitung der kristallographischen Strukturaufklärung wurden an einigen leicht zugänglichen Vertretern die Gitterkonstanten, das Zellvolumen V, die Auslöschungen auf Grund von Weissenberg- und Präzessionsaufnahmen und danach die möglichen Raumgruppen sowie die Röntgendichte D_R ermittelt. Die Ergebnisse dieser Untersuchungen sind in der Tabelle 1 zusammengestellt. Neben den erwähnten Daten findet man in der zweiten Spalte einen Literaturhinweis auf die Darstellung der betreffenden Substanz. In der vierten Spalte ist die experimentelle Dichte D_{exp} und das Dipolmoment Δ [Debye] zusätzlich angegeben, soweit sie gemessen wurden oder aus der Literatur bekannt sind.

Vom 6-Dimethylamino-6-morpholinofulven existieren zwei Phasen (*a*) und (*b*), die unter Nr. 3 und Nr. 4 in der Tabelle 1 aufgeführt sind.

Die Strukturaufklärung an den Substanzen Nr. 1, 5 und 12 (s. Tabelle 1) ist in Angriff genommen.

Tabelle 1. *Kristallographische Daten und Dipolmomente substituierter Fulvene*

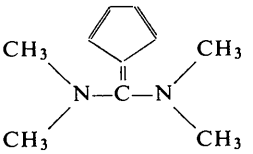
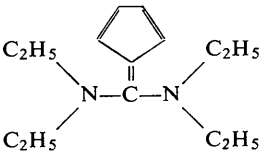
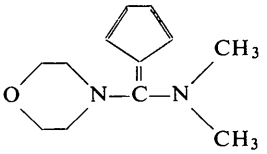
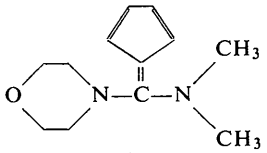
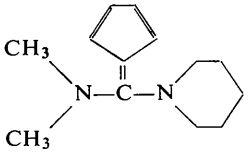
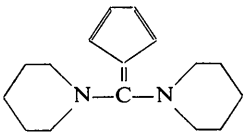
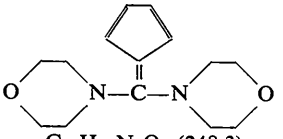
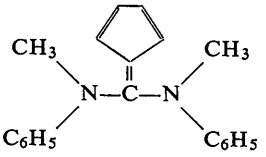
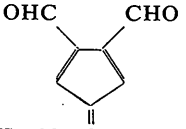
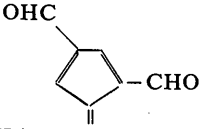
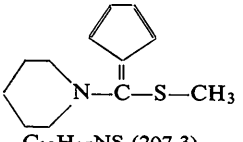
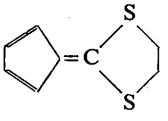
Nr.	Formel Molekulargewicht Literatur	Gitterkonstanten Zellvolumen Mögl. Raumgruppen	Z = Moleküle pro Zelle D_R, D_{exp}, Δ	Auslöschungen WB = Weissenberg PR = Präzession	
1	 $C_{10}H_{16}N_2$ (164,3) (Hafner, Schulz & Wagner, 1964; Hartke, 1964)	$a_o = 13{,}41 \pm 0{,}04$ Å $b_o = 7{,}85 \pm 0{,}03$ $c_o = 9{,}42 \pm 0{,}03$ $V = 990$ Å^3 $Pnma$–D_{2h}^{16} $Pn2_1a$–C_{2v}^9	$Z = 4$ $D_R = 1{,}101$ $D_{exp} = 1{,}108$ $\Delta = 5{,}4$–$5{,}45$	$h1l$: — $h0l$: — $hk0$: $h = 2n$ $0kl$: $k + l = 2n$ $h00$: $h = 2n$ $0k0$: $k = 2n$ $00l$: $l = 2n$	WB WB WB WB
2	 $C_{14}H_{24}N_2$ (220,4) (Salamon, 1969)	$a_o = 17{,}5 \pm 0{,}1$ Å $c_o = 25{,}4 \pm 0{,}1$ $V = 6730$ Å^3 $R3c$–C_{3v}^6 $R\bar{3}c$–D_{3d}^6	$Z = 18$ $D_R = 0{,}98$ $D_{exp} = 0{,}99$	$hk0$; $hk1$; $hk2$; $hk3$; $0kl$; $1kl$; hkl: $-h + k + l = 3n$ hhl: $l = 2n$	WB WB WB
3	 (*a*) $C_{12}H_{18}N_2O$ (206,3) (Salamon, 1969)	$a_o = 17{,}66 \pm 0{,}06$ Å $b_o = 8{,}25 \pm 0{,}03$ $c_o = 17{,}00 \pm 0{,}06$ $\beta = 107{,}0°$ $V = 2395$ Å^3 $P2_1/c$–C_{2h}^5	$Z = 8$ $D_R = 1{,}152$ $D_{exp} = 1{,}12$	$h1l$: — $h0l$: $l = 2n$ $hk0$: — $0k0$: $k = 2n$	WB WB WB
4	 (*b*) $C_{12}H_{18}N_2O$ (206,3) (Salamon, 1969)	$a_o = 14{,}80 \pm 0{,}05$ Å $b_o = 8{,}48 \pm 0{,}04$ $c_o = 9{,}36 \pm 0{,}04$ $V = 1183$ Å^3 $P2_12_12_1$–D_2^4	$Z = 4$ $D_R = 1{,}16$	$h1l$: — $h0l$: — $hk0$: — $0kl$: — $h00$: $h = 2n$ $0k0$: $k = 2n$ $00l$: $l = 2n$	WB WB WB WB
5	 $C_{13}H_{20}N_2$ (204,3) (Salamon, 1969)	$a_o = 10{,}88 \pm 0{,}04$ Å $b_o = 9{,}50 \pm 0{,}04$ $c_o = 11{,}68 \pm 0{,}04$ $V = 1200$ Å^3 $P2_12_12_1$–D_2^4	$Z = 4$ $D_R = 1{,}13$	$h1l$: — $h0l$: — $0kl$: — $h00$: $h = 2n$ $0k0$: $k = 2n$ $00l$: $l = 2n$	WB WB WB
6	 $C_{16}H_{24}N_2$ (244,4) (Salamon, 1969)	$a_o = 16{,}42 \pm 0{,}05$ Å $b_o = 9{,}96 \pm 0{,}04$ $c_o = 8{,}62 \pm 0{,}03$ $V = 1410$ Å^3 $Pbam$–D_{2h}^9 $Pba2$–C_{2v}^8	$Z = 4$ $D_R = 1{,}15$ $\Delta = 5{,}6$	$h1l$: — $h0l$: $h = 2n$ $hk0$: — $0kl$: $k = 2n$ $h00$: $h = 2n$ $0k0$: $k = 2n$ $00l$: —	WB WB WB WB

Tabelle 1 (*Fort.*)

Nr.	Formel Molekulargewicht Literatur	Gitterkonstanten Zellvolumen Mögl. Raumgruppen	Z = Moleküle pro Zelle D_R, D_{exp}, Δ	Auslöschungen WB = Weissenberg PR = Präzession	
7	 $C_{14}H_{20}N_2O_2$ (248,3) (Salamon, 1969)	a_o = 9,76 ± 0,03 Å b_o = 8,52 ± 0,03 c_o = 15,77 ± 0,05 V = 1312 Å^3 *Pnma*–D_{2h}^{16} *Pn*2$_1$*a*–C_{2v}^9	Z = 4 D_R = 1,26	1*kl*: — 0*kl*: $k+1=2n$ *h*0*l*: — *hk*0: $h=2n$ *h*00: $h=2n$ 0*k*0: $k=2n$ 00*l*: $l=2n$	*WB* *WB* *WB* *WB*
8	 $C_{20}H_{20}N_2$ (288,4) (Salamon, 1969)	a_o = 10,68 ± 0,04 Å b_o = 11,62 ± 0,04 c_o = 13·25 ± 0,05 V = 1654 Å^3 *Pbcn*–D_{2h}^{14}	Z = 4 D_R = 1,15 D_{exp} = 1,17 Δ = 3,5	*hk*1: — *hk*0: $h+k=2n$ 0*kl*: $k=2n$ *h*0*l*: $l=2n$ *h*00: $h=2n$ 0*k*0: $k=2n$ 00*l*: $l=2n$	*WB* *WB* *PR* *PR*
9	 $(CH_3)_2N—C—N(CH_3)_2$ $C_{12}H_{16}N_2O_2$ (220,3) (Salamon, 1969)	a_o = 14,42 ± 0,03 Å b_o = 8,75 ± 0,03 c_o = 19,37 ± 0,04 V = 2444 Å^3 *Pbcn*–D_{2h}^{14}	Z = 8 D_R = 1,20	*h*1*l*: — *h*0*l*: $l=2n$ *hk*0: $h+k=2n$ 0*kl*: $k=2n$ *h*00: $h=2n$ 0*k*0: $k=2n$ 00*l*: $l=2n$	*WB* *WB* *WB* *WB*
10	 $(CH_3)_2N—C—N(CH_3)_2$ $C_{12}H_{16}N_2O_2$ (220,3) (Salamon, 1969)	a_o = 9,51 ± 0,03 Å b_o = 16,38 ± 0,05 c_o = 7,54 ± 0,03 β = 90,4° V = 1179 Å^3 *P*2$_1$/*c*–C_{2h}^5	Z = 4 D_R = 1,17	*h*1*l*: — *h*0*l*: $l=2n$ *hk*0: — 0*k*0: $k=2n$	*WB* *WB*
11	 $C_{12}H_{17}NS$ (207,3) (Hartke, Schmidt, Castillo & Bartulin, 1966)	a_o = 14,20 ± 0,04 Å b_o = 9,28 ± 0,03 c_o = 9,84 ± 0,03 β = 116,6° V = 1160 Å^3 *P*2$_1$/*a*–C_{2h}^5	Z = 4 D_R = 1,19 Δ = 4,5	*h*1*l*: — *h*0*l*: $h=2n$ *hk*0: — *hk*1: — 0*k*0: $k=2n$	*WB* *WB* *WB* *WB*
12	 $C_8H_8S_2$ (168,3) (Gompper & Kutter, 1965; Hartke, Schmidt, Castillo & Bartulin, 1966)	a_o = 5,82 ± 0,03 Å b_o = 6,72 ± 0,03 c_o = 11,39 ± 0,04 β = 114,6° V = 403 Å^3 *Pc*–C_s^2 *P*2/*c*–C_{2h}^4	Z = 2 D = 1,39	*h*1*l*: — *h*0*l*: $l=2n$ *hk*0: — 0*k*0: —	*WB* *WB* *WB*

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On the crystal structure of leucophanite.

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(*Received* 28 *October* 1968)

The space group and the structure parameters of leucophanite given in a previous paper are confirmed.

In a previous paper (Cannillo, Giuseppetti & Tazzoli, 1967) the space group $P2_12_12_1$ was assumed for the determination of the crystal structure of leucophanite. Some features of the measured intensities led to the conclusion that the true space group would have been $P1$.

In order to resolve the question, the collection of the intensities has been repeated and extended to one half of the reciprocal sphere for Cu $K\alpha$ radiation. The refinement with the least-squares method has been continued in the space group $P1$.

However, the atomic shifts from orthorhombic symmetry were not significant and the variations in the thermal parameters did not suggest another kind of order for the calcium and sodium atoms.

At this stage the suspicion arose that some double reflexion effects were responsible for the 'anomalies' in the measured intensities. Precession pictures taken with Mo $K\alpha$ radiation did not show the previously observed 'anomalies', thus confirming the suspicion; in particular, the three reflexions $h00$ (h odd), inconsistent with the orthorhombic space group, did not appear and the sensible differences between some intensities which would be equivalent in the orthorhombic space group, were not now observed.

Thus the space group of leucophanite is, without any doubt, $P2_12_12_1$, and the structure parameters published in the cited paper are substantially confirmed.

Reference

CANNILLO, E., GIUSEPPETTI, G. & TAZZOLI, V. (1967). *Acta Cryst.* **23**, 255.

Acta Cryst. (1969). B**25**, 993

A comment on the synthesis and lattice constants of transition metal thioniobates with berthierite ($FeSb_2S_4$) structure.

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(*Received* 23 *August* 1968)

Transition metal thioniobates (MNb_2S_4 where M = Mn, Fe, Co, Ni or Cu) have been indexed on the basis of a hexagonal unit cell. The results are much more satisfactory than those from earlier indexing on the basis of an orthorhombic unit cell.

Eibschütz, Hermon & Shtrikman (1967) describe the preparation and X-ray patterns of the compounds MNb_2S_4 (M = Mn, Fe, Co, Ni, and Cu). The X-ray powder photographs of these compounds were indexed on the basis of an orthorhombic unit cell having about the same lattice constants as those published for berthierite ($FeSb_2S_4$) by Buerger & Hahn (1955). Eibschütz *et al.* consider this as evidence that the compounds MNb_2S_4 are isostructural with $FeSb_2S_4$.

These conclusions do not seem to be completely justified. If MNb_2S_4 is isostructural with $FeSb_2S_4$, it would be expected that their X-ray patterns should be very similar, because the scattering powers of Nb and Sb differ by only twenty per cent. Comparing the data of Eibschütz *et al.* with the diagram of $FeSb_2S_4$ published by Buerger (1936), it is easily seen that this is not at all the case.

This discrepancy can be resolved by indexing the published data on the basis of hexagonal unit cells. The lattice