

Fig. 3 shows a projection of the structure of DCT along [010]. Within an upper limit of 4 Å the reference molecule I at x, y, z is surrounded by 12 neighbours at:

- $x, \pm 1 + y, z$ (not shown in Fig. 3);
- $-x, \pm \frac{1}{2} + y, -z$ (II);
- $\pm 1 + x, y, z$ (III);
- $-1 - x, \pm \frac{1}{2} + y, -z$;
- $-x, \pm \frac{1}{2} + y, 1 - z$;
- $-1 - x, \pm \frac{1}{2} + y, 1 - z$.

The shortest intermolecular distances (3.19 Å) are found between O(3) at x, y, z and S(4) at $-x, \frac{1}{2} + y, -z$. All other intermolecular contacts are larger than 3.4 Å.

We wish to express our thanks to Dr H. F. van Woerden for providing the crystals of DCT and to Mr R. A. G. de Graaff for his assistance with the calculations.

References

- ALTONA, C. (1964). Thesis, Leiden.
- ALTONA, C., GEISE, H. J. & ROMERS, C. (1966). *Rec. Trav. chim. Pays-Bas*, **85**, 1197.
- ALTONA, C., HAGEMAN, H. J. & HAVINGA, E. (1968). *Rec. Trav. chim. Pays-Bas*. In the press.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
- BOND, W. L. (1959). In *International Tables for X-ray Crystallography*, Vol. III. Birmingham: Kynoch Press.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
- CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
- DAWSON, B. (1960). *Acta Cryst.* **13**, 403.
- ERIKS, K. & MACGILLAVRY, C. H. (1954). *Acta Cryst.* **7**, 430.
- GEISE, H. J., ROMERS, C. & RUTTEN, E. W. M. (1966). *Acta Cryst.* **20**, 249.
- GEISE, H. J. (1967). *Rec. Trav. chim. Pays-Bas*, **87**, 362.
- LIDE, D. R. JR. (1962). *Tetrahedron*, **17**, 125.
- SHEARER, H. M. M. (1959). *J. Chem. Soc.* p. 1394.
- STEEMAN, J. W. & MACGILLAVRY, C. H. (1954). *Acta Cryst.* **7**, 402.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- WESTRIK, R. & MACGILLAVRY, C. H. (1941). *Rec. Trav. chim. Pays-Bas*, **60**, 794.
- WESTRIK, R. & MACGILLAVRY, C. H. (1954). *Acta Cryst.* **17**, 764.
- WOERDEN, M. F. VAN & HAVINGA, E. (1967a). *Rec. Trav. chim. Pays-Bas*, **86**, 341.
- WOERDEN, M. F. VAN & HAVINGA, E. (1967b). *Rec. Trav. chim. Pays-Bas*, **86**, 353.

Acta Cryst. (1968). **B24**, 1477

Possible Close-Packed Ordered Structures Related to MoNi₄

BY PAUL A. BECK

Department of Metallurgy, University of Illinois, Urbana, Illinois 61801, U.S.A.

(Received 28 July 1967 and in revised form 15 January 1968)

The geometric conditions of periodic stacking of ordered close-packed layers of the type occurring in MoNi₄ are investigated, and a method is described for the systematic generation of such layer structures with a given number of layers in the primitive unit cell.

Several ordered close-packed structures of the AB₃ composition are known to be related to the AuCu₃ structure in the sense that they consist of ordered layers identical with those in AuCu₃, but stacked in a different way. The best known among these AB₃ structure types are the following: MgCd₃ (h.c.p. stacking, *ab*, of ordered layers; Dwight & Beck, 1959), TiNi₃ (La-stacking, *abcb*, of ordered layers; Laves & Wallbaum, 1939), VCo₃ (stacking of ordered layers, *abcacb*; Saito, 1959) and Ta(Pd, Rh)₃ (Sm-stacking, *abcbcacab*, of ordered layers; Giessen & Grant, 1959).^{*} General procedures, which may be used to derive all geometrically possible stacking variants based on a given num-

ber of stackings of a certain layer in systems with a connectivity of two or four, were described recently (Beck, 1967). The ordered close-packed layer of composition AB₄, of which the MoNi₄ structure (Harker, 1944) may be built, was described by Beattie (1967) and it is shown in Fig. 1. Stacking variants based on this layer, and having up to seven-layers, are systematically derived in the following by adapting to this more complicated system the method previously outlined (Beck, 1967).

In Fig. 1 the two-dimensional primitive unit mesh of the close-packed ordered layer is outlined. In the MoNi₄ structure both layers adjacent to the one shown in the Figure (the latter is characterized by Mo atoms on sites *a*, i.e. by 'stacking position *a*') have Mo atoms placed over (or under) one of the four interstitial sites designated 0, 9, 7 and 2 in Fig. 1. Thus, the nearest

^{*} Some of the structures mentioned actually are slightly distorted. For the purposes of the present paper this may be disregarded.

neighbors to a Mo atom are Ni atoms in the adjacent layers, as well as in its own layer. Of the four stacking operators corresponding to the stacking positions mentioned, the one producing the stacking displacement from *a* to 0 (indicated by arrow in Fig. 1) is designated *p*. The inverse operator *p*⁻¹ produces a displacement from *a* to 9, operator *q* gives a lateral displacement from *a* to 7 and its inverse *q*⁻¹ from *a* to 2, all of them shown by arrows in Fig. 1. In the MoNi₄ structure only one of these stacking operations is utilized, and it is repeated from each layer to the next. Repeated action of operator *p* results in the following stacking positions for successive layers: *a* 0 1 *b* 2 3 *c* 4 5 *d* 6 7 *e* 8 9 (as one can readily see in Fig. 1). The stacking position following 9 is *a* and a new cycle of stacking positions starts. Thus, viewing the three-dimensional ordered close-packed structure of MoNi₄ in the direction *normal* to the close-packed layer, the stacking cycle consists of fifteen layers. In a unit cell based on the close-packed layer, and on the direction normal to it, fifteen layers would have to be represented. However, since all the stacking displacements from layer to layer are identical, it is clear that, by using the line connecting the center of the Mo atom in position *a* with that in the next layer located above position 0, a very much smaller primitive unit cell, containing only one Mo and four Ni atoms, can be constructed. Because of its small size, in this paper the primitive unit cell will be used, even though its symmetry is only triclinic.*

Since the four operators are crystallographically equivalent, using *p*⁻¹, *q* or *q*⁻¹ instead of *p* in setting up a one-layer primitive unit cell leads to the same result. Referring to Fig. 1, the successive stacking positions generated by operator *q* are the following: *a* 7 4 *b* 9 6 *c* 1 8 *d* 3 0 *e* 5 2. When viewed in the direction normal to the layer, this stacking cycle, as well as the corresponding ones generated by operators *p*⁻¹ and *q*⁻¹, again consists of fifteen layers. By making use of two or more of the operators *p*, *p*⁻¹, *q* and *q*⁻¹, it is possible for a given number of layers in the primitive cell to identify and to derive systematically all possible layer structures of the type considered. As in the case of MoNi₄, the primitive cells for many of these structures (but by no means for all) are then found to be nonorthogonal.† In the following, the structures with orthogonal primitive cells will be discussed first; this will be followed by a discussion of the structures with nonorthogonal primitive cells.

* The unit cell most commonly used in describing the MoNi₄ structure is not the primitive one, but the tetragonal unit cell shown in Fig. 2, containing ten atoms. A set of the close-packed ordered layers is outlined in the Figure. For the purposes of crystal analysis by diffraction the larger size of this unit cell is outweighed by its higher symmetry.

† The terms *orthogonal structure* and *nonorthogonal structure* are used in this paper to designate layer structures for which the primitive unit cell may be based on the two-dimensional unit mesh in the close packed ordered layer, shown in Fig. 1, combined with the direction *normal* to the layer, or with a direction *inclined* to the layer, respectively.

Considerations relating to orthogonal primitive cells

In view of the closing of the stacking cycle in the direction normal to the layer after fifteen consecutive applications of either one of the four operators, one may write

$$p^{15}=1, p^{-15}=1, q^{15}=1 \text{ and } q^{-15}=1. \quad (1)$$

As may be seen by examining the stacking sequences given above for the *p* and *q* operators, a closed stacking cycle also results from the four times repeated operation of *p* combined with a single operation of *q*:

$$p^4 \cdot q=1, \text{ and by analogy } p^{-4} \cdot q^{-1}=1, \\ p \cdot q^4=1 \text{ and } p^{-1} \cdot q^{-4}=1. \quad (2)$$

Equations (1) and (2) represent algebraic rules imposed on the stacking operators by the structure of the AB₄ layer considered (Fig. 1), by the requirement of close packing between layers and by the stipulation of an

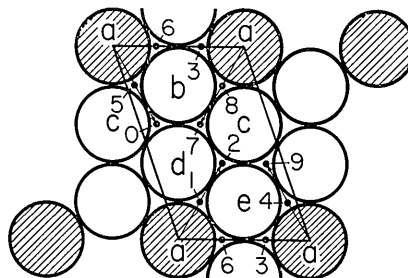


Fig. 1. Close-packed ordered layer of composition AB₄. A atoms (at sites *a*) have only B nearest neighbors. Stacking positions of A atoms in parallel layers are located over numbered sites (which are 'interstitial' in layer *a*) and over lettered sites (occupied in layer *a*). If ordering is disregarded, the lettered, the even-numbered and the odd-numbered sites correspond to sites *a*, *b* and *c*, respectively, in the 'basic structure'. A atoms in an adjacent layer (in an ordered structure), placed over sites 0, 7, 2 and 9, have only B atom neighbors in layer *a*. Vectors *a*0, *a*7, *a*2 and *a*9 represent possible stacking displacements between adjacent layers, compatible with the requirement of all-B coordination for A atoms.

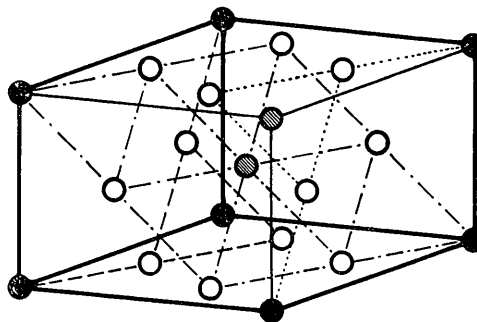


Fig. 2. Tetragonal unit cell of MoNi₄. Inclined close-packed ordered layers (as shown in Fig. 1) are indicated by dashed, dotted and dash-dot lines.

all-B coordination polyhedron around each A atom. From these rules the condition of closure of the stacking cycle and, thus, the geometrically possible structure-types related to MoNi_4 can be deduced for the general case of combinations of two or more of the four stacking operators.

With the layer and the stacking operators under consideration, the general condition of closure of a stacking cycle in N layers, when viewed in the normal direction, is:

$$p^{x'} \cdot p^{-x''} \cdot q^{y'} \cdot q^{-y''} = 1 \text{ or } p^{x'-x''} \cdot q^{y'-y''} = 1, \quad (3)$$

where

$$x' + x'' + y' + y'' = N. \quad (4)$$

The non-negative integers x' , x'' , y' and y'' give the number of operations of each of the four stacking operators p , p^{-1} , q and q^{-1} , respectively, within a single stacking cycle. If $x' - x'' = x$ and $y' - y'' = y$, then equation (3) may be written as:

$$p^x \cdot q^y = 1,$$

and from equation (2)

$$q = p^{-4},$$

so that one may write:

$$p^{x-4y} = 1. \quad (5)$$

According to equations (1) equation (5) is satisfied if, and only if,

$$x - 4y = 15k \text{ or } y - 4x = 15m, \quad (6)$$

where k and m are integers. Thus, (6) represents the *general condition of closure* for orthogonal structures.

The algebraic rules expressed in equations (1) and (2) are invariant with respect to the following transformations:

- A. $p \rightarrow q, q \rightarrow p, p^{-1} \rightarrow q^{-1}$ and $q^{-1} \rightarrow p^{-1}$ or
 B. $p \rightarrow q^{-1}, q^{-1} \rightarrow p, p^{-1} \rightarrow q$ and $q \rightarrow p^{-1}$ or
 C. $p \rightarrow p^{-1}, p^{-1} \rightarrow p, q \rightarrow q^{-1}$ and $q^{-1} \rightarrow q.$ (7)

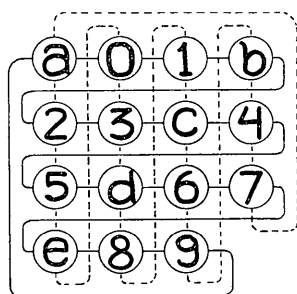


Fig. 3. Layer connection diagram, with layers designated by numbered and lettered stacking positions, as in Fig. 1. Those stacking positions that may be occupied by adjacent layers are directly connected by (continuous or dotted) lines. A closed stacking cycle, viewed in the direction normal to the layer, corresponds to a closed line in the graph.

If the operators describing a particular set of stacking sequences are subjected to any of the above transformations, the new set of stacking sequences and the structure defined by the transformed operators are crystallographically equivalent to the original ones. The transformations A , B and C represent the formation of mirror images or a 180° rotation of the stacking vectors with respect to the layer (Fig. 1). When deriving the different possible structures related to MoNi_4 by interleaving and permutating the operators (Beck, 1967), these criteria must be used, along with those given previously (Beck, 1967), in eliminating duplication.

The conditions prevailing in the system under consideration can be readily visualized with the help of the layer connection diagram given in Fig. 3. Each stacking position is designated by a letter or number, as in Fig. 1, and those which may be adjacent to one another are directly connected by a line. The continuous line (horizontal) corresponds to stacking operator p (when the line is followed from left to right) and to p^{-1} (when followed from right to left). The dotted line (vertical) corresponds to stacking operator q (going upward) and to q^{-1} (going downward). A closed stacking cycle is represented in the diagram by a closed line ('stacking graph') composed, in general, of portions of both the continuous and dotted lines. The stacking graph may be self intersecting and it may have sections superimposed on one another. The greater complexity of the system investigated, as compared with those previously studied (Beck, 1967), is shown by the large (topological) connectivity number of 17, appropriate to the graph (layer connection diagram) in Fig. 3. Transformations A , B and C , discussed above, correspond to reflection in diagonal mirrors, or to inversion of the stacking graph with respect to the layer connection diagram (Fig. 3).

Derivation of orthogonal primitive cells

In the following, each orthogonal primitive unit cell is described by giving the sequence of operators in the shortest cycle generating the structure.

$N=1$. There is no orthogonal one-layer structure, since all four operators, when applied singly, result in lateral displacement.

$N=2$. It is clear that the only two-layer structure that satisfies the condition of closure, equation (6), is one for which $x=0$ and $y=0$ (with $k=m=0$). Here a stacking displacement according to either p or q is followed by the inverse stacking displacement. The structure can be described in terms of a primitive monoclinic unit cell with 10 atoms in the two layers. The corresponding 'basic structure' ('Unterstruktur', ordering disregarded; see Schubert, 1964) is hexagonal close packed: $\dot{a}\dot{b}$.

$N=3$. Equations (1) and (2) show that the smallest odd number of layers giving a complete stacking cycle is $N=5$. The stacking cycle can not be closed in three

layers and, therefore, a three-layer orthogonal unit cell is geometrically not possible.

$N=4$. The condition of closure allows the following four different stacking variants:

Operators	Stacking positions	Basic structure
$ppp^{-1}p^{-1}$	$a010$	$abc\bar{b}$
$pqp^{-1}q^{-1}$	$a0e\bar{7}$	$\bar{a}bac$
$pp^{-1}qq^{-1}$	$a0a\bar{7}$	$\bar{a}ba\bar{c}$
$pqq^{-1}p^{-1}$	$a0e0$	$\bar{a}b$

$N=5$. The only possible structure of this type corresponds to p^4 , $q=1$, equation (2). The stacking positions are $a01b\bar{2}$. The corresponding basic structure is $\bar{a}bcab$.

$N=6$. The condition of closure permits the following stacking variants:

Operators	Stacking positions	Basic structure
p^3p^{-3}	$a01b1\bar{0}$	$\bar{a}bcacb$
p^3q^{-3}	$a01b4\bar{7}$	$\bar{a}bc$
$p^2p^{-2}pp^{-1}$	$a010a\bar{0}$	$\bar{a}bcba\bar{b}$
$p^2q^{-2}pq^{-1}$	$a01c6\bar{7}$	$\bar{a}bc$
$p^2p^{-2}qq^{-1}$	$a010a\bar{7}$	$\bar{a}bcba\bar{c}$
$p^2qp^{-2}q^{-1}$	$a018e\bar{7}$	$\bar{a}bcba\bar{c}$
$p^2p^{-2}q^{-1}q$	$a010a\bar{2}$	$\bar{a}bcba\bar{b}$
$pp^{-2}pqq^{-1}$	$a0a9a\bar{7}$	$\bar{a}baca\bar{c}$
$pp^{-2}pq^{-1}q$	$a0a9a\bar{2}$	$\bar{a}bacab$
$pp^{-2}ppq^{-1}$	$a0a96\bar{7}$	$\bar{a}bacb\bar{c}$
$pp^{-2}q^{-1}pq$	$a0a9b\bar{2}$	$\bar{a}bacab$
$pp^{-1}pp^{-1}qq^{-1}$	$a0a0a\bar{7}$	$\bar{a}babac$
$pp^{-1}pp^{-1}q^{-1}q$	$a0a0a\bar{2}$	$\bar{a}b$
$pp^{-1}pqp^{-1}q^{-1}$	$a0a0e\bar{7}$	$\bar{a}babac$
$pp^{-1}qpp^{-1}q^{-1}$	$a0a7e\bar{7}$	$\bar{a}baca\bar{c}$
$pp^{-1}qpq^{-1}p^{-1}$	$a0a7e\bar{0}$	$\bar{a}bacab$
$pp^{-1}qp^{-1}pq^{-1}$	$a0a76\bar{7}$	$\bar{a}bacb\bar{c}$
$pq^{-1}pq^{-1}pq^{-1}$	$a03c6\bar{7}$	$\bar{a}bc$
$pp^{-1}q^{-1}p^{-1}pq$	$a0a2b\bar{2}$	$\bar{a}b$

$N=7$. The following stacking variants are compatible with the condition of closure:

Operators	Stacking positions	Basic structure
p^5qp^{-1}	$a01b23\bar{0}$	$\bar{a}bcabc\bar{b}$
p^4qpp^{-1}	$a01b2a\bar{0}$	$\bar{a}bcabab$
$p^3qp^2p^{-1}$	$a01b9a\bar{0}$	$\bar{a}bcacab$
$p^4q^2q^{-1}$	$a01b2a\bar{7}$	$\bar{a}bcba\bar{c}$
$p^4qq^{-1}q$	$a01b2a\bar{2}$	$\bar{a}bcabab$
p^3qpq^{-1}	$a01b9a\bar{7}$	$\bar{a}bcaca\bar{c}$
$p^3qpq^{-1}q$	$a01b9a\bar{2}$	$\bar{a}bcacab$
$p^3q^2pq^{-1}$	$a01b96\bar{7}$	$\bar{a}bcacb\bar{c}$
$p^3qq^{-1}pq$	$a01b9b\bar{2}$	$\bar{a}bcacab$
$p^2qp^2qq^{-1}$	$a0189a\bar{7}$	$\bar{a}bcba\bar{c}$
$p^2qp^2q^{-1}q$	$a0189a\bar{2}$	$\bar{a}bcba\bar{b}$
$p^2q^2p^2q^{-1}$	$a018d6\bar{7}$	$\bar{a}bcba\bar{b}\bar{c}$
p^2qpqpq^{-1}	$a01896\bar{7}$	$\bar{a}bcba\bar{b}\bar{c}$
$p^2qpq^{-1}pq$	$a0189b\bar{2}$	$\bar{a}bcba\bar{b}$

It is interesting to note that, in spite of the complexity of the system, the number of stacking variants for two to five layers is relatively low (a total of 6, as compared with the two- to five-layer total of 4 for the much simpler AB₃ system in Appendix I of the previous paper (Beck, 1967). However, the large number of six- and seven-layer stacking variants (33 as compared with 6 in the AB₃ system, suggests that at larger layer numbers the greater complexity makes itself felt much more fully.

Considerations relating to structures with non-orthogonal cells

In analogy to the primitive cell for MoNi₄, discussed above, many other stacking variants with non-orthogonal primitive cells may be constructed. The primitive cell is uniquely described by the set of stacking operators forming the shortest repeat cycle in the sequence of operators appropriate to the structure. All structures for which this set does *not* satisfy the condition of closure for orthogonal cells, equation (6), are non-orthogonal. For instance, for MoNi₄ the 'stacking cycle' consists of a single operator: p as discussed above. For any other non-orthogonal structure, as well as for MoNi₄, it is possible to construct a larger orthogonal cell. But for the purposes of the present study it is more convenient to use the smaller non-orthogonal primitive unit cell.

In deriving systematically the various possible stacking sequences for non-orthogonal structures by permutation and interleaving (Beck, 1967), the same criteria may be used for eliminating duplication as those discussed above in connection with the orthogonal structures.

Derivation of non-orthogonal primitive cells

$N=1$. Operator:

p The other three operators yield crystallographically equivalent results. This is the MoNi₄-type structure. The basic structure is: $\bar{a}bc$.

$N=2$. Operators:

pq Equivalent to orthogonal structure with $N=10$, resulting from a sequence of five repetitions of the pair of operators as seen in this stacking sequence: $\bar{a}0e8d6c4b\bar{2}$. Basic structure: $\bar{a}b$.

pq^{-1} Equivalent to orthogonal structure with $N=6$, which is obtained by three times repeated action of the pair of operators, as shown in the stacking sequence: $\bar{a}03c6\bar{7}$. Basic structure: $\bar{a}bc$.

For the same number of layers the number of non-orthogonal stacking variants is much larger than the number of orthogonal ones. For the sake of brevity, in the rest of this tabulation only the sequence of

operators is given for each primitive unit cell up to $N=5$.

$N=3$. p^2p^{-1} , p^2q , p^2q^{-1} ; $pp^{-1}q$.

$N=4$. p^3p^{-1} , p^3q , p^3q^{-1} ; p^2q^2 , p^2q^{-2} ;
 $p^2p^{-1}q$, $p^2p^{-1}q^{-1}$, p^2qq^{-1} ;
 $pp^{-1}pq$, $pp^{-1}pq^{-1}$, $pqpq^{-1}$, $pqp^{-1}q$, $pq^{-1}p^{-1}q^{-1}$,
 $pp^{-1}qp^{-1}$, $pq^{-1}qq^{-1}$, $pp^{-1}q^{-1}p^{-1}pqq^{-1}q$.

$N=5$. p^4p^{-1} , p^4q^{-1} ; p^3p^{-2} , p^3q^2 , p^3q^{-2} ;
 $p^3p^{-1}q$, $p^3p^{-1}q^{-1}$, p^3qq^{-1} ; $p^2p^{-2}q$, $p^2p^{-2}q^{-1}$, $p^2q^2p^{-1}$,
 $p^2q^2q^{-1}$, $p^2q^{-2}p^{-1}$, $p^2q^{-2}q$;
 $p^2p^{-1}pq$, $p^2p^{-1}pq^{-1}$, p^2qpq^{-1} , $p^2p^{-1}pp^{-1}$, p^2qpq ,
 $p^2q^{-1}pq^{-1}$, $p^2p^{-1}qp^{-1}$, $p^2qp^{-1}q$, $p^2q^{-1}qq^{-1}$,
 $p^2q^{-1}p^{-1}q^{-1}$, $p^2p^{-1}q^{-1}p^{-1}$, $p^2p^{-1}qq^{-1}$,
 $p^2qp^{-1}q^{-1}$, $p^2qq^{-1}p^{-1}$, $p^2qq^{-1}q$;
 $pp^{-1}pp^{-1}q$, $pqpqp^{-1}$, $pq^{-1}pq^{-1}q$, $pp^{-1}pp^{-1}q^{-1}$,
 $pp^{-1}pqq^{-1}$, $pp^{-1}pqp^{-1}$, $pp^{-1}q^{-1}pq$, $pqpqq^{-1}$,
 $pq^{-1}pq^{-1}p^{-1}$.

H. Beattie of the General Electric Company kindly contributed stimulating discussion. Professor D.P. Shoemaker made a very useful suggestion. This work was supported by a grant from the Army Research Office (Durham).

References

- BEATTIE, H. J. (1967). In *Intermetallic Compounds*, edited by J. H. WESTBROOK, p. 152. New York: John Wiley.
 BECK, P. A. (1967). *Z. Kristallogr.* **124**, 104.
 DWIGHT, A. E. & BECK, P. A. (1959). *Trans. AIME*, **215**, 976.
 GIESSEN, B. C. & GRANT, N. J. (1965). *Acta Cryst.* **18**, 1080.
 HARKER, D. (1944). *J. Chem. Phys.* **12**, 315.
 LAVES, F. & WALLBAUM, H. J. (1939). *Z. Kristallogr.* **A101**, 78.
 SAITO, S. (1959). *Acta Cryst.* **12**, 500.
 SCHUBERT, K. (1964). *Kristallstrukturen Zweikomponentiger Phasen*. Berlin: Springer-Verlag.

Acta Cryst. (1968). **B24**, 1481

The Crystal Structures of 9-Dicyanomethylenefluorene Derivatives.

II. 9-Dicyanomethylene-2,7-dinitrofluorene

BY J. SILVERMAN, A. P. KRUKONIS AND N. F. YANNONI

Energetics Branch, Space Physics Laboratory, Air Force Cambridge Research Laboratories, Bedford, Massachusetts 01730, U.S.A.

(Received 9 November 1967)

9-Dicyanomethylene-2,7-dinitrofluorene crystallizes in the orthorhombic space group $Pnna$. There are four molecules with twofold point group symmetry in the unit cell: $a=19.26$, $b=11.19$, $c=6.33$ Å. An intense reflection in conjunction with packing considerations provided sufficient information to solve the structure. A refinement by least-squares based on 613 reflections from X-ray photographs converged at an R value of 8.9%. The fluorene moiety is planar; nitro groups are rotated out-of-plane by 17.6° and the dicyanomethylene portion is rotated slightly about its formal double bond. In the herringbone packing scheme, the presence of weak self-complexing by charge transfer is suggested by the association among parallel molecules which includes π -orbital overlap between outer benzenoid rings and close approaches of 3.33 and 3.37 Å for $C \cdots C$ and 3.15 Å for $O \cdots C$. Comparisons with the recently reported structure of the 2,4,7-trinitro derivative induce some speculations as to the connection between structural and electrical properties of the two compounds and, in particular, lead to a postulated relationship between the high photoconductivity of the present molecule and its weak self-complexing.

Introduction

9-Dicyanomethylene-2,7-dinitrofluorene (DDF) is one of a series of new electron acceptors, nitro derivatives of fluorene- $A^{9\alpha}$ -malononitrile, synthesized by T.K. Mukherjee of our laboratory. The relative photoconductive response of polycrystalline samples as well as the order of electron affinities among the several molecules has been determined (Mukherjee, 1966, 1968). Crystallographic results on the 2,4,7-trinitro derivative (DTF) were presented as part I of this series (Silverman, Krukoni & Yannoni, 1967). Here,

we report on the structure of the 2,7-dinitro derivative, and based on a comparison with the DTF structure, offer some speculations as to the connection between the structural and electrical properties.

Experimental

Crystal data

9-Dicyanomethylene-2,7-dinitrofluorene (DDF)
 $C_{16}H_6N_4O_4$, $M=318.2$; m.p. = $298-299^\circ\text{C}$.
 Orthorhombic, $a=19.26$, $b=11.19$, $c=6.33$ (based on $\lambda=0.7017$ Å and with e.s.d.'s of 0.3%).