Solid State Conformation of N-Substituted Amides. I. Crystal Structure of 4-Diethylcarbamoyl-1-cyclohexene-5-carboxylic Acid

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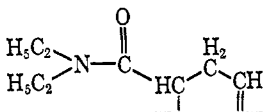
Abstract: 4-Diethylcarbamoyl-1-cyclohexene-5-carboxylic acid crystallizes in the orthorhombic Pbca space group, with $a = 22.611$, $b = 11.526$, and $c = 9.607$ Å. The structure has been solved by the method of the maximum probability of a set of signs described by Allegra and Valle. The $(C_{\alpha})_2N{-}C'(=O)C$ group deviates considerably from planarity; one of the C atoms bonded to the N is 0.36 Å out of the mean plane through the other five atoms. The average dihedral angle between the planes $N{-}C_{\alpha}{-}C_{\beta}$ and $C_{\alpha}{-}N{-}C'$ is 89 ± 6° showing a large deviation from the minima currently attributed to the torsional energy function around $N{-}C_{\alpha}$. The cyclohexene ring is found in the half-chair conformation. Hydrogen bonds are formed between carboxyl and carbonyl groups of different molecules.

In connection with crystallographic studies on molecules containing amide groups in progress in our laboratory,[2] we have undertaken the determination of the crystal structure of 4-diethylcarbamoyl-1-cyclohexene-5-carboxylic acid (DCCA).



Although some conformational studies in solution have been performed on N,N-dialkylamides[3-5] no structural determination in the solid state has been reported to the best of our knowledge.

Experimental Section

DCCA was purchased from Eastman Organic Chemicals and crystallized from acetone solutions. A Picker four-circle automated diffractometer equipped with a PDP-8 digital computer was used for the collection of 2114 independent reflections, of which 1769 were well above the background intensity. The determination of the lattice constants was carried out by a least-squares refinement of the setting angles (2θ, ω, and χ) of 12 reflections ($2\theta > 90°$, Cu Kα radiation, λ 1.5418). On the basis of the systematic absences the space group was found to be Pbca; the resulting crystal data are reported in Table I. Integrated intensities were collected using the θ–2θ scan mode and a scan angle of 1.5° was found to be sufficient for all the reflections over the range of 2θ examined (0–130°). Two stationary-crystal–stationary-counter background counts of 10 sec were taken at each end of each scan.[6]

Table I. Crystal Data

4-Diethylcarbamoyl-1-cyclohexene-5-carboxylic acid, $C_{12}H_{19}O_3N$
Mol wt = 225.29
Orthorhombic, space group Pbca, $Z = 8$, $F(000) = 976$
$a = 22.611 \pm 0.008$ Å
$b = 11.526 \pm 0.003$ Å
$c = 9.607 \pm 0.003$ Å
$d_{\text{calcd}} = 1.195$ g/cm^3

Structure Determination and Refinement

The structure of DCCA was solved with the aid of a direct method for sign determination proposed by one of us[7] based on the maximization of the $\Pi(s_1, s_2, s_3, \ldots)$ function.[8,9] Twenty-four basic reflections with $|E| > 2.2$ were chosen and the 11 sign combinations with highest Π values were recognized to differ only in few signs (to a maximum of five) strongly favoring the hypothesis that the true solution was within them. Starting from the first combination we generated signs of reflections with $|E| \geq 1.2$ with the aid of the Sayre's relations and the strongest 14 peaks in the resulting Fourier map could be attributed to 14 out of the 16 nonhydrogen atoms of the asymmetric unit. The whole molecule could then be easily recognized in the subsequent Fourier synthesis and the atomic parameters were isotropically refined through six full-matrix least-squares cycles to an R $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ factor of 0.12. After four cycles following the introduction of anisotropic thermal parameters the final R value is 0.076 for the 1769 nonzero reflections (0.090 for all 2114 measured reflections). The hydrogen atoms were introduced in their sterically expected positions ($d_{C-H} = 1.08$, $d_{O-H} = 1.00$ Å, $\angle H{-}C{-}H = 109°$ and $\angle C{-}O{-}H = 120°$) in the last cycle of the refinement process; their parameters were held fixed with an isotropic thermal factor equal to the average of the B_{ii}'s of the carrier atom. The weighting scheme adopted corresponds to that suggested by Cruickshank:[10] $w(hkl) = 1/(aF_o^2(hkl) + bF_o(hkl) + c)$. In Table II the fractional coordinates and the thermal factors are reported to-

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(2) (a) E. Benedetti, P. Corradini, M. Goodman, and C. Pedone, *Proc. Nat. Acad. Sci. U. S.*, **62**, 650 (1969); (b) E. Benedetti, P. Corradini, and C. Pedone, *Biopolymers*, **7**, 751 (1969); (c) E. Benedetti, P. Corradini, and C. Pedone, *J. Phys. Chem.*, **73**, 289 (1969).

(3) R. M. Hammaker and B. A. Guggler, *J. Mol. Spectrosc.*, **17**, 356 (1965).

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(6) A complete set of crystallographic FORTRAN IV programs written by Immirzi were used: A. Immirzi, *Ric. Sci.*, 1967, **37**, 743, 846, 850 (1967). All the computations were carried out at the Computer Center of the Polytechnic Institute of Brooklyn (IBM 360/50).

(7) G. Allegra, *Acta Crystallogr.*, **19**, 949 (1965).

(8) G. Allegra and S. Valle, *ibid.*, **25**, 107 (1969).

(9) A. Braibanti, A. Manotti Lanfredi, A. Tiripicchio, and F. Logiudice, *ibid.*, **25**, 93 (1969).

(10) D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press Ltd., New York, N. Y., 1961, p 31.

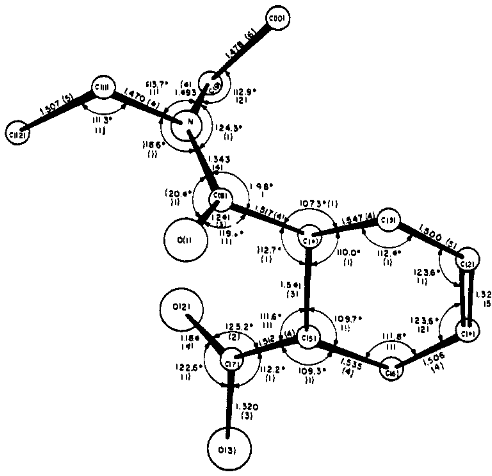


Figure 1. Molecular model of DCCA. Bond distances and angles are reported, together with the corresponding error standard deviations, in units of the last significant digit.

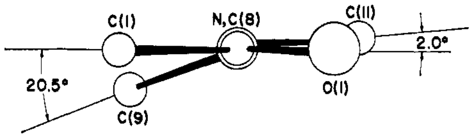


Figure 2. View of the amide group along the N–C(8) bond. The internal rotation angles are indicated (*cf.* Table III; esd ≃ 0.7°).

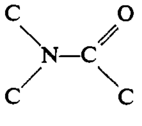
gether with the corresponding standard deviations. A list of observed and calculated structure factors has been deposited as Document No. NAPS-00811 with the American Society for Information Science. (A copy may be obtained by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies to ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N.Y. 10022.)

Discussion of the Structure

(A) Molecular Conformation

The molecular model of DCCA is reported in Figure 1, where the bond lengths and angles are also indicated. A list of the internal rotation angles is given in Table III. The main features of the molecular conformation are discussed below.

(1) The bonding about the nitrogen atom is significantly nonplanar; the distance of N from the plane containing C(8), C(9), and C(11) is 0.100 ± 0.004 Å. Consequently the amide group



is also nonplanar. The dihedral angle between the least-squares planes through N—C(=O)C and C_2N—C is 11.4°. The relative equations and mean square distances (msd) are, respectively

$$0.3640x + 0.6667y + 0.6504z - 8.1856 = 0 \qquad \text{msd} = 0.014\ \text{Å}$$

$$0.4632x + 0.7367y + 0.4926z - 8.9893 = 0 \qquad \text{msd} = 0.042\ \text{Å}$$

Table II. Final Atomic Parameters

(A) Position Parameters			
Atom	x	y	z
C(1)	0.5296 (1)	0.4055 (3)	0.1807 (3)
C(2)	0.5145 (1)	0.4868 (3)	0.2707 (3)
C(3)	0.4518 (1)	0.5216 (3)	0.2989 (3)
C(4)	0.4082 (1)	0.4732 (2)	0.1893 (3)
C(5)	0.4229 (1)	0.3456 (2)	0.1583 (3)
C(6)	0.4855 (1)	0.3366 (2)	0.0975 (3)
C(7)	0.3790 (1)	0.2929 (2)	0.0580 (3)
C(8)	0.3462 (1)	0.4894 (2)	0.2461 (3)
C(9)	0.3201 (1)	0.6280 (3)	0.0550 (4)
C(10)	0.3541 (2)	0.7369 (3)	0.0627 (5)
C(11)	0.2540 (1)	0.5950 (3)	0.2609 (3)
C(12)	0.2073 (2)	0.5127 (4)	0.2090 (4)
O(1)	0.3293 (1)	0.4303 (2)	0.3464 (2)
O(2)	0.3380 1)	0.3417 (2)	0.0089 (3)
O(3)	0.3915 (1)	0.1841 (2)	0.0294 (2)
N	0.3114 (1)	0.5728 (2)	0.1940 (3)
H(1)C(1)[a]	0.577	0.383	0.166
H(1)C(2)	0.550	0.532	0.324
H(1)C(3)	0.438	0.489	0.402
H(2)C(3)	0.448	0.616	0.303
H(1)C(4)	0.414	0.523	0.092
H(1)C(5)	0.421	0.296	0.257
H(1)C(6)	0.500	0.246	0.094
H(2)C(6)	0.485	0.370	−0.008
H(1)C(9)	0.277	0.647	0.006
H(2)C(9)	0.343	0.568	−0.016
H(1)C(10)	0.362	0.780	−0.029
H(2)C(10)	0.397	0.718	0.117
H(3)C(10)	0.331	0.797	0.139
H(1)C(11)	0.240	0.685	0.241
H(2)C(11)	0.259	0.587	0.374
H(1)C(12)	0.165	0.529	0.257
H(2)C(12)	0.221	0.425	0.230
H(3)C(12)	0.202	0.523	0.096
H(1)O(3)	0.366	0.140	−0.037

(B) Anisotropic Thermal Parameters[b]						
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	4.2 (1)	6.2 (1)	6.3 (1)	−0.2 [1)	−1.0 (1)	0.6 (1)
C(2)	5.3 (1)	6.2 (1)	6.0 (1)	−1.2 (1)	−1.2 (1)	0.1 (1)
C(3)	5.7 (1)	5.2 (1)	5.6 (1)	−0.5 (1)	−0.9 (1)	−1.1 (1)
C(4)	4.7 (1)	3.6 (1)	3.8 (1)	0.1 (1)	−0.2 (1)	−0.1 (1)
C(5)	4.3 (1)	3.7 (1)	3.7 (1)	0.2 (1)	−0.5 (1)	−0.1 (1)
C(6)	4.5 (1)	4.8 (1)	5.5 (1)	0.7 (1)	−0.3 (1)	−0.3 (1)
C(7)	5.0 (1)	4.1 (1)	3.9 (1)	0.3 (1)	−0.6 (1)	−0.1 (1)
C(8)	5.2 (1)	3.6 (1)	3.9 (1)	0.3 (1)	−0.2 (1)	−0.1 (1)
C(9)	6.5 (1)	6.2 (1)	5.9 (1)	1.4 (1)	0.6 (1)	1.5 (1)
C(10)	12.8 (3)	5.1 (2)	9.8 (2)	1.4 (2)	3.8 (3)	2.0 (2)
C(11)	5.1 (1)	5.4 (1)	5.6 (1)	1.1 (1)	0.9 (1)	0.1 (1)
C(12)	5.7 (2)	8.7 (2)	5.7 (2)	−0.1 (2)	−0.3 (1)	0.5 (2)
O(1)	5.6 (1)	6.0 (1)	4.5 (1)	0.8 (1)	0.3 (1)	1.7 (1)
O(2)	9.9 (2)	6.3 (1)	11.4 (2)	2.7 (1)	−6.6 (2)	−2.7 (1)
O(3)	6.9 (1)	4.3 (1)	6.4 (1)	0.4 (1)	−1.7 (1)	−1.4 (1)
N	5.7 (1)	4.3 (1)	4.8 (1)	1.2 (1)	0.9 (1)	0.9 (1)

[a] H(*n*)X(*m*) stands for hydrogen number (*n*) bonded to X(*m*).
[b] Temperature factor in the form $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

The resulting geometry is reported in Figure 2. It is worth noting that five out of the six atoms of the amide group are approximately coplanar while C(9) deviates by 0.36 Å from the least-squares plane through the other atoms. A pyramidal bonding around the nitrogen atom has already been proposed on the basis of microwave data for formamide[11] as well as for other noncarboxylic amides like nitramide and cyanamide[12] in the gaseous state. To the best of our knowledge no evidence of significant deviation from planarity has ever

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[11] C. C. Costain and J. H. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).
[12] J. K. Tyler, J. Sheridan, and C. C. Costain, unpublished work cited by P. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

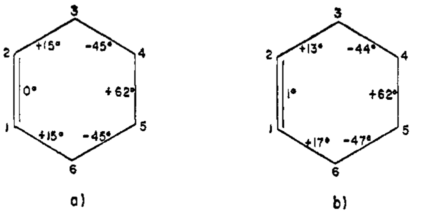

Figure 3. Comparison of the internal rotation angles of the cyclohexene ring predicted (a) and found (b) in the present investigation.

been reported for carboxylic amides in the crystalline state except in the case of the cyclic dipeptide of L-alanine, where the dihedral angle around the N–C deviates by 8° from the value corresponding to planarity.[2] The angle between the C(8)–N axis and the bisector of C(9)–N–C(11) is 11° in our case (to be compared with the value of 17° reported for the corresponding angle in gaseous formamide[11]).

Table III. Internal Rotation Angles[a]

C(1)–C(2)–C(3)–C(4)	13.0
C(2)–C(3)–C(4)–C(5)	−43.9
C(3)–C(4)–C(5)–C(6)	61.8
C(4)–C(5)–C(6)–C(1)	−47.3
C(5)–C(6)–C(1)–C(2)	16.6
C(6)–C(1)–C(2)–C(3)	1.1
C(2)–C(3)–C(4)–C(8)	−166.9
C(6)–C(5)–C(4)–C(8)	178.4
C(1)–C(6)–C(5)–C(7)	170.2
C(7)–C(5)–C(4)–C(8)	−56.8
C(5)–C(4)–C(8)–O(1)	−51.2
C(3)–C(4)–C(8)–O(1)	70.1
C(4)–C(5)–C(7)–O(2)	0.5
C(4)–C(5)–C(7)–O(3)	179.3
C(6)–C(5)–C(7)–O(3)	−57.6
C(6)–C(5)–C(7)–O(2)	122.2
C(4)–C(8)–N–C(9)	20.5
C(4)–C(8)–N–C(11)	173.5
O(1)–C(8)–N–C(9)	−164.1
O(1)–C(8)–N–C(11)	1.9
C(8)–N–C(9)–C(10)	95.3
C(8)–N–C(11)–C(12)	83.4

[a] *trans* conformation = 180°. The average estimated standard deviation is 0.7°.

(2) The second relevant feature of the structure is the conformation of the N–$(C_2H_5)_2$ group. The dihedral angles which characterize the C(8)–N–C(9)–C(10) and the C(8)–N–C (11)–C(12) sequences are 95.3 ± 1 and 83.4 ± 1°, respectively. These figures differ from the values of the conformational minima around the N–C_α bond in polypeptide chains proposed by either Brant and Flory[13] or Scott and Scheraga;[14] the disagreement could be explained assuming, according to the above authors, a low value of the rotational barrier around these bonds (of the order of 1 kcal/mol or less) so that the packing forces can play an essential role in determining the molecular conformation. On the other hand, the conformation found by us is also in disagreement with the surprising planar arrangement proposed for N,N-diethylacetamide by Hammaker and Guggler[8] from nmr measurements.

(3) The cyclohexene ring is in the half-chair conformation predicted earlier by Beckett, Freeman, and Pitzer[15] and subsequently confirmed by X-ray results on different molecules, such as morphine[16] and the *cis,-trans,cis*-1,3,4,5,6 isomer of pentachlorocyclohexene.[17] The symmetry of the ring is very closely C_2; the agreement between our experimental values of the dihedral angles on the ring and those predicted by Bucourt on the basis of minimum energy calculations[18] is remarkable (Figure 3); the presence of two *trans* substituents in positions 4 and 5 apparently does not affect the minimum energy conformation of the ring.

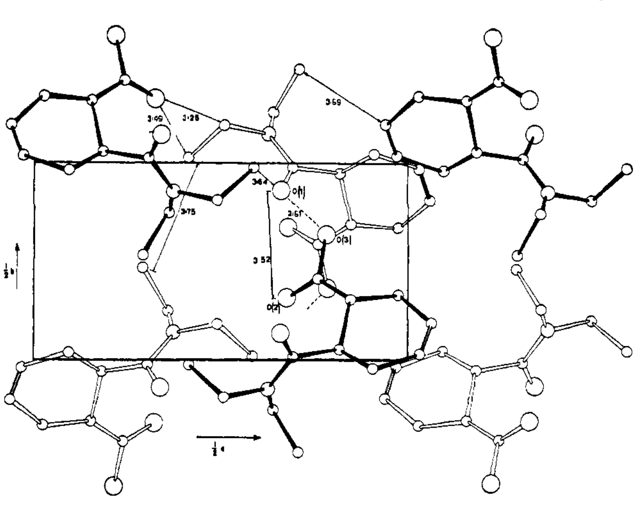

Figure 4. Molecular packing of DCCA along (001). The shortest intermolecular contacts are reported.

(4) The orientation of the carboxyl group is such that the ketonic group C(7)–O(2) is in the preferred *syn* planar conformation with respect to one of the cyclohexene C–C bonds (C(4)–C(5)), as it has often been found by other authors[19] and recently by some of us.[20,21] It is worth noting that this conformation is achieved in spite of a relatively short C(8)–O(2) intramolecular distance (2.85 Å) between atoms four bonds apart. The carboxyl group C—C(=O)—O appears to be quite planar, and the equation of the least-squares plane containing the four atoms is

$$-0.5680x - 0.2938y + 0.7688z + 5.4356 = 0$$

with a msd for all the atoms of 0.001 Å.

The esd's given in Figure 1 have been calculated neglecting vibrational motion effects, which could play some role in inducing an additional error in the geometrical parameters. This may be particularly true where atoms which display markedly anisotropic thermal factors are involved, such as C(10), C(12), and O(2) (see Table II). The geometrical differences between the two ethyl groups may be partly attributed to such effects.

(B) Crystal Packing

The mode of packing may deserve a short discussion. In Figure 4 a view of the structure along (001) is shown.

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(17) R. A. Pasternak, *ibid.*, **4**, 316 (1951).

(18) R. Bucourt, *Bull. Soc. Chim. Fr.*, 2080 (1964).

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(20) E. Benedetti, P. Corradini, C. Pedone, and B. Post, *Chem. Commun.*, 1626 (1968); *J. Amer. Chem. Soc.*, **91**, 4072 (1969).

(21) E. Benedetti, P. Corradini, and C. Pedone, *ibid.*, **91**, 4075 (1969).

The shortest intermolecular contacts are reported. The structure consists of hydrogen-bonded rows of molecules, the hydrogen bonds being formed between molecules related by a glide plane. The O(3)···O(1) distance between hydrogen-bonded atoms (see Figure 4) is 2.6 Å; the distance between O(1) and the least-squares plane containing the C—C(=O)—O group of atoms (see the end of the previous paragraph) is 0.16 Å. The O(2) atom not involved in hydrogen bonding is characterized by a large thermal motion, as might be expected (see Table II). As observed in most molecular crystals, the values of the thermal parameters reflect a significant increase of the thermal motion of the more peripheral atoms (*cf.* thermal factors of C(10) and O(2)).

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Symmetry Classification and Selection Rules for Some Electron Donor–Acceptor Complexes

George R. Anderson

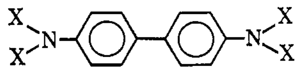
Contribution from the Laboratory of Physical Chemistry, Groningen University, The Netherlands, and the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received December 9, 1969*

Abstract: The structure and electronic spectra of molecular complexes composed of π-electron donor (D) and acceptor (A) molecules are discussed. Based upon estimates of low-lying π-electron orbital symmetries, complex stabilization due to charge-transfer delocalization in the DA pair is allowed or can be ruled out for specific configurations of the complex. These results are tabulated for a number of D and A molecules possessing D_{2h} symmetry (Tables VI–IX). DA complexes for which structural data are known are all found to have correct symmetries for charge-transfer stabilization from the lowest lying D^+A^- electronic state. The spectra of DA complexes follow the selection rules given by group theory in the point group to which the complex belongs. There are seven different ways to arrange D and A molecules so that they share together at least one element of symmetry (Figure 1). From the representations of the charge-transfer states given in Tables VI–IX for the various D–A molecular configuration, one may easily predict which charge-transfer transitions are allowed and the axes of polarization. Previously known spectra are discussed. When polarization data are reported, assignments are discussed and some additional DA structural information is advanced for the solids. In the case of Amano, Kuroda, and Akamatu's recent findings, two (not one) charge-transfer bands are reported for several DA complex solids for which the axes of polarization are perpendicular relative to each other. Their interesting results can be explained on the basis of D and A molecular orbital symmetries and selection rules based on possible orientations of the complex.

The spectroscopic observations recently reported by Amano, Kuroda, and Akamatu[1] on the polarization of charge-transfer (CT) bands of some crystalline electron donor–acceptor complexes give cause for the following paper. Their spectra of a series of eight solids showed the presence of two low-lying CT bands in the frequency range below the first expected π → π transition of either donor or acceptor molecules. Their account of the spectral positions and spacings of the two CT bands was sound and in line with previous observations made in solution.

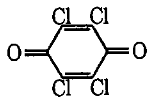
The polarization axes of the first and second CT bands, however, were not always parallel relative to one another, and in four of the eight solids studied the first and second CT bands were perpendicular relative to one another. This result was discussed in the paper but not adequately resolved. In contrast to the analysis of Amano, Kuroda, and Akamatu, an alternative explanation of their spectra is presented here with a more general discussion of the symmetry of DA complexes and the possible selection rules that result from group theoretical considerations.

The anomalous polarization results were reported for the four DA complex solids composed of benzidine and N,N,N′,N′-tetramethylbenzidine

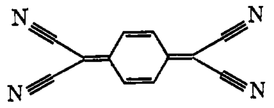


(X = Me or H)

and the two acceptor molecules, chloranil



and 7,7,8,8-tetracyanoquinodimethane (TCNQ).



All four molecules belong to the D_{2h} point group; the coordinate axis applied to each molecule has the z axis normal to the paper, y and x axes vertical and horizontal, respectively. Thin platelets of the complex were

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[1] T. Amano, H. Kuroda, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **42**, 671 (1969).