1,2,3,4,9,12,13,14-Octahydro-10,11-benzofluoranthrene.—Eighteen grams of phosphorus tribromide diluted with 10 cc. of dry benzene were dropped into an ice-cooled solution of 20 g. of 2-tetralol[7] in 5 cc. of benzene. The product was left for six hours at room temperature, washed with ice-cooled water and a sodium bicarbonate solution, then it was diluted with 50 cc. of dry ether and dried a day long on sodium sulfate. When distillation under reduced pressure was attempted, a product distilled with b. p. 130–150° at 10 mm., which showed a bromine content of 14% instead of 37.9%, proving decomposition with elimination of hydrobromic acid.

The ether–benzene solution of 2-bromotetralin, prepared as indicated above, was treated with 2 g. of magnesium and 250 cc. of dry ether in the usual manner and after complete dissolution was treated with a mixture of 8 g. of 1-tetralone in 80 cc. of ether. After the usual procedure, the solvent was removed and the remaining product was steam distilled. The residual oil was extracted with benzene, the solution dried and the benzene was removed. The residue (10 g.) was heated with 15 g. of phosphorus pentoxide at 130–140°. After washing with water and extraction with benzene, an oil was obtained whose main part (4–5 g.) distilled in the range of 195–197° at 1 mm. After ten days the distillate deposited colorless needles which recrystallized from ethanol showed the m. p. 150.5°. The mixed melting point with the hydrocarbon obtained by the procedures described above did not give any depression.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.57; H, 8.49.

By the dehydrogenation with palladium–charcoal 10,11-benzofluoranthrene was obtained in yellow needles, melting at 165°; the picrate melts at 195°.

Attempted Synthesis of the Hydrocarbon $C_{20}H_{20}$ with M. p. 93°.—Starting with 1-tetralole,[7] 1-bromotetralin was prepared, which was transformed into the corresponding magnesium derivative and treated with 1-tetralone, in a manner quite similar to that described above. The oil obtained after treatment with phosphorus pentoxide gave the b. p. 203–204° at 2 mm. After one day it deposits a small amount of colorless crystals referred to later. The oil left after the filtration of these crystals did not crystallize any more during the following six weeks. By dehydrogenation with palladium–charcoal it gave, in good yield, 10,11-benzofluoranthrene, identified by m. p., mixed m. p. and picrate.

1,1'-Ditetralyl.—The crystals obtained above as a secondary reaction product, after being recrystallized from ethanol, showed the m. p. 83°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.54; H, 8.45. Found: C, 91.30; H, 8.70.

By dehydrogenation for an hour with palladium–charcoal in an atmosphere of carbon dioxide, colorless crystals of m. p. 157° were obtained. The mixed melting point with 1,1'-bis-naphthyl,[10] gave no depression.

Summary

1 It has been shown, by synthesis, that the hydrocarbon $C_{20}H_{20}$ with m. p. 150.5°, which was obtained by Dansi and Ferri[2] by the action of aluminum chloride on 1,2,3,4-tetralin, is 1,2,3,4-9,12,13,14-octahydro-10,11-benzofluoranthrene.

2. The hydrocarbon $C_{20}H_{20}$ with m. p. 93°, obtained by von Braun and Kirschbaum[1] by the polymerization of 1,2-dialin with sulfuric acid is very probably 5,6,7,8,9,12,13,14-octahydrobenzofluoranthrene.

3. It has been shown by six different syntheses that the hydrocarbon $C_{20}H_{12}$ which is formed by the dehydrogenation of the preceding hydrocarbons, is 10,11-benzofluoranthrene.

BUCHAREST, ROUMANIA RECEIVED JUNE 30, 1948[11]

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(10) Prepared according to E. Sakellarios and Th. Kyrmis. *Ber.*, **57**, 324 (1924).

(11) Delayed because of difficulty of communication.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

The Molecular Structure of N-Methylacetamide

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In the present paper we report the experimental results of the Raman effect, infrared absorption, ultraviolet absorption and dipole moment observed for N-methylacetamide, $CH_3CONHCH_3$, which is the simplest molecule containing the peptide bond and hence can be regarded as a structural unit of the polypeptide chain. A sample prepared by Dr. Kanji Mayumi and Ichiro Okano was subjected several times to vacuum distillation and was used in this experiment (m. p. 28°).

Raman Effect and Infrared Absorption in the Rock Salt Region

The experimental results of the Raman effect and infrared absorption for the liquid at ordinary temperature are shown in Table I.[1] As to the Raman effect the measurement was also made for the liquid at 90–95°, for the aqueous solution (*p*H = 4), and for the acidic solution (hydrochloric acid, *p*H = 1). The result obtained was essentially the same as in the case for the liquid at ordinary temperature. We can, therefore, consider that N-methylacetamide consists of only one kind of molecule, otherwise the spectrum would change at higher temperature or in solutions.

The skeleton of this molecule consists of five atoms (C, O and N atoms) and, therefore, the skeletal frequencies number $3 \times 5 - 6 = 9$. As shown in Table I, we have observed almost the expected number of skeletal frequencies and we thus have another reason to believe that there is only one kind of molecule. The normal vibration calculation[2] which would take too much space

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(1) As to the previous measurement in the liquid state see: Kohlrausch and Seka, *Z. physik. Chem.*, **B43**, 355 (1939).

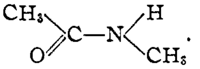
(2) The details will be published elsewhere: see also Simanouti, *J. Chem. Phys.*, **17**, 245, 848 (1949).

to detail here has shown that the skeletal frequencies calculated for the *trans* amide form are in good agreement with the observed values (see the last column of Table I).

TABLE I

RAMAN EFFECT AND INFRARED ABSORPTION OF LIQUID N-METHYLACETAMIDE

Raman effect	Infrared absorption	Vibration type[a]	Calculated skeletal frequencies[b]
290 (2)		δ(CNC)	249
440 (4)		δ(C=O)	477
627 (6)		δ(NCC)	557
738 (1)	710 (7)	π	
883 (8)	880 (5)	ν(C—C)	867
988 (2)	995 (7)	$\delta(CH_3)$	
	1040 (6)	$\nu(N-CH_3)$	1053
	1095 (5)	$\delta(CH_3)$	
1165 (4)	1160 (8)	ν(C—N)	1177
1302 (7b)	1290 (9)	$\delta(CH_3)$	
1370 (3)	1370 (9)	$\delta(CH_3)$	
1413 (4)	1410~	$\delta(CH_3)$	
1450 (3b)	1440 (9)		
	1550 (8)	δ(NH)	
1655 (5b)	1640 (10)	ν(C=O)	1715
2722 (1)			
2808 (2)			
2900 (3b)	2900 (7)	$\nu(CH_3)$	
2835 (6)		$\nu_s(CH_3)$	
2980 (2b)	2960 (8)	$\nu(CH_3)$	
	3100 (9)	ν(NH---O)	
3308 (3bb)	3300 (10)	ν(NH---O)	

[a] ν is the stretching vibration, δ the deformation vibration, and π the perpendicular vibration. [b] Calculated for the *trans* amide form  .

Ultraviolet Absorption

We have observed the ultraviolet absorption of N-methylacetamide in an aqueous solution of the concentration of 0.008 mole/l. No absorption maximum has been found at a wave length longer than 2100 Å. at this concentration. For the dilute acidic solutions practically the same result has been obtained. If, however, the concentration of N-methylacetamide and the acid was raised (*e. g.*, $CH_3CONHCH_3$ 2.0 moles/l. and hydrochloric acid 5.0 moles/l. as shown in Table II), we observed another weak absorption at λ 2695 ± 10. Let us discuss these absorption bands in connection with the band observed at λ 2650 for an aqueous solution of acetone (concentration 0.17 mole/l.).

Let the molecular orbital wave functions of two π electrons of the C=O bond of acetone, approximated by linear combination of the outer shell atomic-orbitals of carbon and oxygen, by φ_0 and φ_1, φ_0 referring to the ground state and φ_1 to the excited state. Then the complete wave functions, *i. e.*, orbital functions multiplied by spin functions α and β, would be $\varphi_0\alpha$, $\varphi_0\beta$, $\varphi_1\alpha$ and $\varphi_1\beta$. In the normal state of the acetone molecule the two π electrons are in $\varphi_0\alpha$ and $\varphi_0\beta$ states and through the absorption at λ 2650 one of the oxygen electrons (lone pair) is transferred to φ_1 state according to McMurry.[3]

For N-methylacetamide in the normal state we shall consider the resonance

$$CH_3C{=}ONHCH_3 \longleftrightarrow CH_3O^-C{=}N^+HCH_3 \qquad (2)$$

which will mean the migration of a pair of nonbonding electrons of the N-atom to $\varphi_1\alpha$ and $\varphi_1\beta$ states, just as in the case of Sklar's treatment of the aniline molecule.[4] In the excited state, however, one of the $\varphi_1\alpha$ and $\varphi_1\beta$ states is already occupied by an electron and, therefore, only one of the two electrons can migrate into the φ_1 state and the resonance energy in the excited state will be smaller than that in the normal state. In other words the energy difference between the normal and the excited states of N-methylacetamide will become larger through the resonance of Eq. 2. If there were no resonance and the molecular state could be represented by a single valence bond structure $CH_3CONHCH_3$, the said energy difference would be equal to that of acetone. Thus we can understand why the absorption frequency of N-methylacetamide was observed at a shorter wave length than that of acetone. Our view stated here is supported by the aforedescribed experiment in which we found another absorption maximum at λ 2695, since this absorption can be reasonaly assigned to N-methylacetamidonium ion whose normal state can approximately be represented by a single valence bond structure $CH_3CON^+H_2CH_3$.

We have good reason to consider that the absorption intensity of N-methylacetamidonium ion is of the same order of magnitude as that of acetone. Hence, if we compare the intensity of absorption at λ 2695 in the acidic solution of N-methylacetamide with that at λ 2650 of acetone, we can obtain the dissociation constant K of the reaction, $CH_3CON^+H_2CH_3 \rightleftarrows CH_3CONHCH_3 + H^+$

$$K = C_2C_3/C_1 \qquad (3)$$

where C_1, C_2 and C_3 denote, respectively, the concentration of $CH_3CON^+H_2CH_3$, $CH_3CONHCH_3$ and H^+. The result of the measurement is shown in Table II.

According to Pauling[5] let us attribute the difference in the dissociation constant K between amine and amide to the resonance energy of the latter. We have then

$$E_r = RT \ln \frac{K[CH_3CON^+H_2CH_3]}{K[(CH_3)_2N^+H_2]} = 16 \text{ kcal./mole} \qquad (4)$$

as shown in Table II. From this value of resonance energy we see that among the intramolecular rotational states about the C–N bond as axis only the *trans* or the *cis* position is favored and

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(3) McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

(4) Sklar, *ibid.*, **7**, 984 (1939).

(5) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., p. 207, 1940.

TABLE II

DISSOCIATION CONSTANT K AT 10° AND RESONANCE ENERGY E_r

Concentrations are expressed in mole/l.

Total concn. of N-methylacetamide, $C_1 + C_2$	Concn. of dissociated form, C_1[a]	Concn. of normal form, C_2	Total concn. of HCl, $C_1 + C_3$	Concn. of H⁺, C_3	K	pK	E_r, (kcal./mole)
2.0	0.10	1.9	5.0	4.9	93	−1.97	16.4
3.0	.17	2.83	4.5	4.33	72	−1.86	16.3
4.0	.10	3.9	4.0	3.9	150	−2.18	16.7

[a] This was obtained from the concentration of acetone which gave the same absorption intensity (at λ 2650) as that of the acidic solution of N-methylacetamide (at λ 2695).

that the hydrogen atom of the NH group tends to form a strong hydrogen bond.[6] Furthermore, we see from the value of $pK = -2$ of Table II that for the solution of $p\text{H} = 0$ the number of molecules in the dissociated form $CH_3CON^+H_2$-CH_3 amounts only to one per cent. of that in the normal form $CH_3CONHCH_3$. This would be the reason why we have observed only the Raman lines assigned to the latter form even in a strongly acidic solution.

Dipole Moment

The dipole moment of N-methylacetamide has been observed in carbon tetrachloride solutions between 15 and 40° with results shown in Table III, from which we see that the value of molecular polarization P becomes smaller as the concentration is lowered.[7] This would be explained from the assumption that N-methylacetamide forms associated molecules with larger moment. The fact that the apparent moment decreases with rising temperature also supports this view (see Table III).

TABLE III

MOLECULAR POLARIZATION P AND DIPOLE MOMENT μ OF N-METHYLACETAMIDE

Solvent	Temp., °C.	Weight fraction of solute	P, cc.	μ, D
CCl_4	15	0.001491	654	5.44
		.004265	942	6.56
		.005806	1015	6.82
CCl_4	25	.000585	510	4.8
		.001491	540	5.02
		.00195	610	5.34
		.004265	849	6.33
		.005806	925	6.62
CCl_4	40	.001496	497	4.93
		.004266	730	6.01
Dioxane	20.1	.00249	400	
		.00398	385	
		.00435	382	
			P_∞ = 423	4.39

From the aforedescribed *trans* and *cis* forms we can consider the structures of associated molecules as shown in Fig. 1 in which the dotted lines denote the hydrogen bond. Of these the structure (I) is quite similar to that of the carboxylic acid dimer, for which the molecular polarization should become larger with decreasing concentration.[8] This is not compatible with the result of the present experiment and we should adopt (II) as the structure of associated molecules and therefore, the *trans* form as the structure of single molecule in conformity with the experimental result of the infrared absorption to be described below.

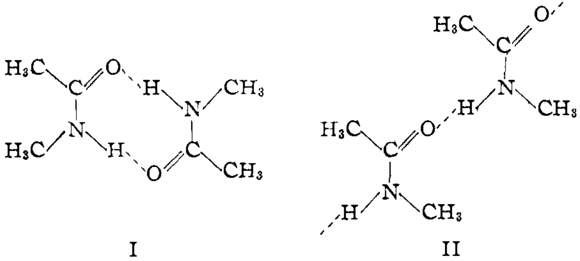

Fig. 1.—Associated molecules of N-methylacetamide.

We have also made a dipole measurement in dioxane which tends to dissociate the molecular complex formed by hydrogen bond into single molecules. As shown in Table III we have here a normal polarization–concentration relation from which we obtain the molecular polarization extrapolated to infinite dilution (P_∞ = 423 cc.) and the moment of a single molecule (μ = 4.39 D), taking the sum of atomic and electronic polarizations as 19 cc.

The moment value calculated by simple vector addition for N-methylacetamide in planar form amounts to 3.47 D for the *trans* form and to 2.43 D for the *cis* form. Practically the same values (3.34 and 2.44 D, respectively) are obtained if we consider that each of the N–H and N–CH_3 bonds makes an angle of 30° with the C–C–N plane. To compare these values with the experimental ones we have to take into account the abnormality of dioxane solution, the resonance effect of Eq. (2), and the induction effect. The contribution of these factors may be estimated as 1.0 D, since the moment value of a similar molecule such as dimethyl or diethyl acetamide in

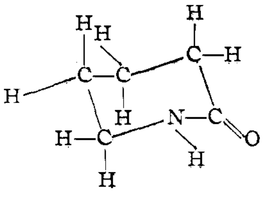

Fig. 2.—The molecular structure of δ-valerolactam.

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[6] For the polypeptide chain we can expect similar resonance, by which we can explain the strong tendency of the polypeptide chain to form intermolecular and intramolecular hydrogen bonds.

[7] For the experimental procedure see *e. g.*, Mizushima, Morino and Higasi, *Sci. Pap. Inst. Phys. Chem. Research* (*Tokyo*), **25**, 159 (1934).

[8] Pohl, Hobbs and Gross, *J. Chem. Phys.*, **9**, 408 (1941).

TABLE IV

ABSORPTION MAXIMA OF N-METHYLACETAMIDE IN THE 3 μ REGION

Molar absorption coefficient is given in parentheses

State		Temp., °C.	ν_{NH} of free molecule, μ	ν_{NH} of associated molecule, μ		ν_{CH}, μ
Gaseous state		210	2.86			3.38
Carbon tetrachloride solution	0.0014 mole/l.	15	2.88(17)			3.38(29)
	.0032 mole/l.	15	2.88(14)	2.97(9)		3.38(28)
	.031 mole/l.	13	2.88(12)	3.00(38)	3.22(18)	3.38(41)
	.031 mole/l.	40	2.88(14)	2.97(15)		3.38(39)
	.079 mole/l.	16	2.88(9)	3.03(35)	3.22(27)	3.38(38)
	.079 mole/l.	39	2.88(9)	2.99(25)	3.22(12)	3.38(33)
Liquid state		*ca.* 30		3.03(73)	3.22(54)	3.38(40)
Crystalline state		*ca.* 10		3.03(69)	3.22(48)	3.38(40)

dioxane is found larger by this amount than that calculated from the simple vector addition.[9] Adding, therefore, 1.0 *D* to the said calculated values, we obtain the moment values 4.4 *D* for the *trans* form and 3.4 *D* for the *cis* form. The observed value 4.39 *D* is in good agreement with that calculated for the *trans* form shown in Fig. 1 (II).

This conclusion is also supported by our dipole measurement made for the molecule of δ-valerolactam which has a ring structure and whose $>$C=O and $>$N–H groups are considered to be in *cis* position to each other (Fig. 2). In carbon tetrachloride solution at 20° we have found the values of apparent moment 2.33, 2.24 and 2.09 *D* for the weight fractions 0.005213, 0.008246 and 0.01384, respectively. The moment is, therefore, much smaller than that of N-methylacetamide and the apparent value increases with decreasing concentration. This would be naturally explained from the said *cis* configuration of the molecule for which we can expect a ring dimer of a form analogous to that shown in Fig. 1 (I).

Our view stated above with regard to the dipole measurement will have more conclusive evidence from the experiment to be described in the next section.

Near Infrared Absorption

The near infrared absorption has been measured in the wave length region between 2.7 and 3.5 μ and between 1.3 and 1.8 μ. For the gaseous N-methylacetamide and from the dilute carbon tetrachloride solution we have observed the absorption maxima at 2.86, 2.88 and 1.48 μ characteristic of the N–H vibration but no absorption between 2.70 and 2.82 μ and between 1.39 and 1.46 μ characteristic of the O–H vibration. From this result we can positively conclude that in the vapor and in dilute non-polar solutions the single molecule of N-methylacetamide is of amide form and not of imidol or enol form having OH group. At higher concentrations, however, 2.88 μ absorption became weaker and at the same time new absorptions were observed at 2.97 $\sim$ 3.03 and 3.22 μ, and in the pure liquid and the crystal the 2.88 μ absorption disappeared. This would be explained by assigning the 2.88 μ band to the N–H vibration of the free molecule and the 2.97 $\sim$ 3.03 and 3.22 μ bands to that of the associated molecule (associated through hydrogen bond). The assignment is also compatible with the result of our observation on a solution of a definite concentration that at higher temperature the 2.88 μ absorption increased its intensity, while the 2.97 $\sim$ 3.03 and 3.22 μ absorptions became weaker.

The observation made in the 1.5 μ region can be explained quite similarly, if we assign 1.48 and 1.52 $\sim$ 1.58 μ bands to the harmonics of 2.88 and 2.97 $\sim$ 3.03 μ bands, respectively. The 1.48 μ absorption due to the free molecule of N-methylacetamide decreased its intensity with increasing concentration, until it disappeared in the pure liquid state, in which only the 1.52 and 1.58 μ absorptions due to the associated molecules were observed. In a solution of a definite concentration the 1.48 μ absorption increased its intensity and at the same time the 1.52 μ and the 1.58 μ absorptions became weaker, as the temperature was raised.

We have already stated that in the rock salt region the C=O absorption of the liquid was observed at 1640 cm.$^{-1}$. In carbon tetrachloride solution this absorption was found to be shifted toward higher frequency (up to 1700 cm.$^{-1}$), as the concentration was lowered. From this fact together with that observed for the N–H vibration stated above we can certainly conclude that the molecular association of N-methylacetamide is caused through the hydrogen bond ($>$N–H---O=C$<$) as shown in Fig. 1.

We have also measured the near infrared absorption of δ-valerolactam and have found the N–H vibration of the free molecule at 2.92 μ, that of associated molecules at 3.11 and 3.24 μ and the C=O vibration of associated molecules at 1660 cm.$^{-1}$. If we compare these absorption bands with those observed for N-methylacetamide, we see, as explained in the following, that the associated molecule of δ-valerolactam is the ring dimer formed of two molecules in the *cis* form, while that of N-methylacetamide is the chain polymer formed of several single molecules in the *trans* form (see Fig. 1 (II)).

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[9] Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934).

(1) That the N–H vibration (2.92 μ) of free δ-valerolactam was found at a longer wave length than that of N-methylacetamide (2.88 μ) would be due to the intramolecular hydrogen bonding of >N–H and O=C< groups situated in the *cis* position in the former molecule. (2) At a concentration of 0.0015 mole/l. in carbon tetrachloride solution δ-valerolactam still showed strong association, while N-methylacetamide was found almost in a unimolecular state. This would be explained from the difference in the strength of hydrogen bond of these two substances, *i. e.*, there is a double hydrogen bond in the ring dimer of δ-valerolactam and the energy of dissociation would be much larger than that of N-methylacetamide whose molecules are connected by a single hydrogen bond (see Fig. 1). (3) When the concentration of the solution was lowered, or its temperature was raised, the wave length of the N–H vibration of the associated molecules of N-methylacetamide was shifted continuously from 3.03 to 2.97 μ and the frequency of C=O vibration from 1640 to 1700 cm.$^{-1}$. This would be due to the chain structure of the associated molecule which may be formed of various numbers of single molecules and, therefore, may show N–H and C=O vibrations of various frequencies. Such a frequency shift has not been observed in the case of δ-valerolactam, the solution of which showed only the change of absorption intensity with the change of concentration and temperature. This can be naturally expected from the type of association of δ-valerolactam for which we have considered only one kind of associated molecule, *i. e.*, the ring dimer.

We want to add a few words about the N–H vibrations of proteins, the measurement of which we have just finished. It was found that the N–H frequencies of egg albumin, serum albumin, etc., are practically the same as those of N-methylacetamide in the liquid state, but they are far different from those of δ-valerolactam. We have, therefore, to consider that in the polypeptide chain the two groups adjacent to the peptide bond (one of them bonded to N–H and the other to C=O) are in general in the *trans* position. This is consistent with the basic structures of the polypeptide chain recently proposed.[10]

Acknowledgment.—We wish to thank Dr. K. Mayumi and I. Okano for the preparation of N-methylacetamide and also K. Hoshino and H. Yumoto for δ-valerolactam. Our thanks are due to Ministry of Education for a grant-in-aid of this research.

Summary

1. The Raman and the infrared spectra of N-methylacetamide can be explained from one molecular configuration of the amide structure. The amount of another configuration is too small to be detected in the vibration spectra.

2. From the measurement of the ultraviolet absorption the molecule was found to resonate between two bond structures $CH_3C{=}ONHCH_3 \leftrightarrow CH_3O^-C{=}N^+HCH_3$, the resonance energy amounting to 16 kcal./mole.

3. Due to this resonance the molecule of N-methylacetamide tends to take either the *cis* form or the *trans* form. The conclusion that this molecule takes only the *trans* form was derived from the comparison of the N–H and C=O vibrations of this molecule with those of δ-valerolactam molecule which is of the *cis* form. The result of the normal vibration calculation and dipole measurement in dioxane is also consistent with this conclusion.

4. It is also due to this resonance that N-methylacetamide has a tendency to form an intermolecular hydrogen bond, through which the polymers of chain structure are formed in the liquid state and in carbon tetrachloride solutions.

5. By comparing the N–H frequencies of some proteins with those of N-methylacetamide in the liquid state the peptide bond of the polypeptide chain was shown to have in general the *trans* form.

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[10] T. Simanouti and S. Mizushima, *Bull. Chem. Soc. Japan*, **21**, 1 (1948). See also Mizushima, Simanouti, Tsuboi, Sugita and Kato, *Nature*, **164**, 918 (1949).