

The Infrared Spectra of Some Simple N-Substituted Amides in the Vapor State

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The vapor absorptions of *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) have been recorded with a prism spectrometer between 4000 cm^{-1} and 415 cm^{-1} . The contour changes resulting from methyl substitution and the consequent increase in asymmetry of the *cis* configuration proposed for *N*-methylformamide, are compared with those in the theoretical contours. As a first approximation, the rigid models for the four molecules are assumed to be valid at the temperatures used. Some of the gross structural features in the spectra are consistent with theory, but the results show the dangers inherent in the use of the theoretical contours as a basis for the detection of minor configurational differences in complex molecules.

I. INTRODUCTION

The infrared absorption band contours for symmetric and asymmetric rotators calculated by Gerhard and Dennison (1) and by Badger and Zumwalt (2), respectively, have been used to determine the configuration of fairly complex molecules in the gaseous state (3-5). There is, however, a great deal of uncertainty attached to the detailed interpretation of such spectra. A simple analysis of the vapor spectrum of methyl formate recorded under prism resolution

showed the *cis* ($\begin{array}{c} \text{O} \quad \text{C} \\ \parallel \quad | \\ -\text{C}-\text{O}- \end{array}$) configuration of the molecule to be the absorbing entity (5). In the case of the closely related *N*-methylformamide, the *cis*

($\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad | \\ -\text{C}-\text{N}- \end{array}$) configuration of the molecule was found to provide a more satisfactory basis for interpreting the vapor spectrum than the *trans* (6), but the greater detail obtained with improved resolution of the 3-4 μ vapor absorption band contours did not allow a simple choice to be made between these two alternative structures (7). A related case is that of formamide where, with the resolution of a silica prism, the 3 μ vapor band contours suggested a nonplanar configuration for the molecule (8), whereas under grating resolution the fine

structure of the same absorptions was found to be consistent with the very nearly planar structure obtained from a detailed microwave study (9, 10). In view of this uncertainty, and the relatively low resolution available, the work described here was done in order to find out whether or not the changes in the observed vapor band contours resulting from further methyl substitution of *N*-methylformamide were consistent with those shown by the theoretical contours.

II. EXPERIMENTAL

A Perkin-Elmer 12C spectrometer converted to double-pass operation and fitted with LiF, NaCl, and KBr prisms, was used to record the spectra. Demountable and fixed path-length cells were used for parallel studies on liquids and solutions. The vapor spectra were obtained using a heated 10-cm cell: the amides were heated in a simple glass reservoir immersed in an oil-bath, and the vapor carried over into the body of the cell by a dry nitrogen stream.

Approximate values for the partial pressure of the vapor in the heated cell were obtained from $\log_{10} P - 1/T$ curves, where P is the vapor pressure in millimeters of the liquid at the absolute temperature T . The curves were drawn using the boiling points and the corresponding vapor pressures available in the literature, and in each case the best fit obtained by the method of least squares. No attempt was made to standardize the rate of flow of nitrogen through the reservoir so that the vapor pressure values given in Fig. 1 are subject to further uncertainty.

DMF and DMA showed signs of decomposition above 150° and 83°C, respectively. The cell temperatures were therefore kept at, or below, these values.

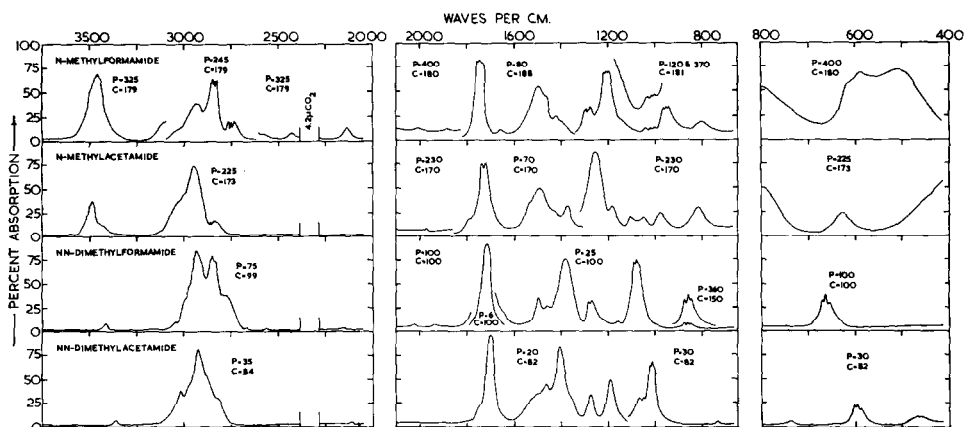


FIG. 1. The infrared vapor spectra of NMF, NMA, DMF, and DMA. P = approximate vapor pressure in mm Hg, T = cell temperature in °C.

The 6μ vapor bands were recorded with the background water-vapor absorptions much reduced by flushing out the spectrometer with a stream of nitrogen. Some additional detail was observed in the spectrum of NMF under these conditions.

The amides were BDH laboratory reagents purified by vacuum distillation, and the carbon tetrachloride and carbon disulfide solvents used to record the solution spectra were purified and redistilled before use. Exposure of the redistilled amides was minimized because of their hygroscopic nature. After exposing capillary films of DMF and DMA to air, new, intense absorptions due to water appeared in the 3μ region of the spectrum (3470 cm^{-1} in DMF, as measured with a rock-salt prism, and 3440 cm^{-1} in that of DMA). These were accompanied by small but definite shifts in a number of other absorptions, those of the carbonyl bands being the more marked— 1677 cm^{-1} to 1667 cm^{-1} in DMF, and 1651 cm^{-1} to 1634 cm^{-1} in DMA.

III. DISCUSSION

A. ASSIGNMENTS

The vapor spectra of the amides are shown in Fig. 1 and the proposed assignments to the fundamental modes of vibration listed in Table I. The designation of these modes as pure bond-stretching or deformation is only approximate, especially in the case of those vibrations which are predominantly skeletal, involving atoms of similar mass and bonds contiguous with others of comparable strength.

Several absorption bands in the monomethylamides show appreciable shifts and changes in relative intensity on dilution in nonpolar solvents as a result of hydrogen-bond breakage, and also in the transition to the vapor phase. These changes simplify the assignment of absorptions due to vibrations mainly confined to the carbonyl and NH bonds. No marked changes in relative intensity or of band position were observed in the spectra of the N,N-disubstituted amides, except in the case of the carbonyl absorptions which shifted from 1677 cm^{-1} in liquid DMF to 1714 cm^{-1} in the vapor—the corresponding shift in DMA being from 1651 cm^{-1} to 1695 cm^{-1} .

The assignment of the fundamental modes of NMF based on dilution, deuteration, and vapor studies in the infrared (6, 11), and on the Raman spectrum (11) must be modified in view of the later studies on C- and N-deuterated NMF by Suzuki (12). The absorption band at 1015 cm^{-1} in the spectrum of liquid NMF has been shown conclusively to arise from a normal mode principally involving the hydrogen atom attached to the formyl carbon, i.e., the out-of-plane mode $\gamma(\text{CH})$. The assignments for NMA have been made with reference to previous studies, and by analogy with the corresponding vibrations in NMF. Thus a previous assignment (13) has been modified, so that bands at 1181, 971,

and 812 cm^{-1} which were attributed to $\nu(\text{C}'\text{—N})$, $\nu(\text{C—C})$, and $\nu(\text{CH}_3)$, respectively, are now assigned to $w(\text{CH}_3)\text{N}$, $\nu(\text{C}'\text{—N})$, and $\nu(\text{C—C})$.

The assignment of the rocking and wagging modes of the methyl groups in DMF and DMA have been made, in the absence of well-established correlations,

TABLE I
Assignments to vapour absorption bands

| NMF | NMA | ASSIGNMENT | DMF | DMA | ASSIGNMENT |
|--------------------------------------|-------------------|--|--|------------------|--|
| 3504 } 3494 } 3482 } 3471 } | 3501 } 3489 } | $\nu(\text{NH})$ | | | |
| 2939 | 3001 } 2940 } | $\nu_{\text{as}}(\text{CH}_3)\text{N}$ | 3000 } 2994 } 2978 } 2946 } 2937 } 2919 } | 2977 } 2934 } | $\nu_{\text{as}}(\text{CH}_3)\text{N}$ |
| | 2880 ^a | $\nu_{\text{as}}(\text{CH}_3)\text{C}$ | | 2870 | $\nu_{\text{as}}(\text{CH}_3)\text{C}$ |
| 2858 } 2847 } 2832 } | | $\nu(\text{CH})$ | 2860 } 2847 } 2834 } | | $\nu(\text{CH})$ |
| | 2830 | $\nu_{\text{s}}(\text{CH}_3)\text{C}$ | | 2824 | $\nu_{\text{s}}(\text{CH}_3)\text{N, C}$ |
| 2763 } 2750 } 2736 } | 2815 | $\nu_{\text{s}}(\text{CH}_3)\text{N}$ | 2783 } 2767 } | | $\nu_{\text{s}}(\text{CH}_3)\text{N}$ |
| 1733 } 1726 } | 1731 } 1713 } | $\nu(\text{CO})$ | 1714 | 1695 | $\nu(\text{CO})$ |
| 1494 | 1497 | $\delta(\text{NH}) + \nu(\text{CN})$ | 1496 | 1492 (sh) | $\nu(\text{CN})$ |
| ~1460 | | $\delta_{\text{as}}(\text{CH}_3)\text{N}$ | | 1465 | $\delta_{\text{as}}(\text{CH}_3)\text{N, C}$ |
| | | | 1457 | | $\delta_{\text{as}}(\text{CH}_3)\text{N}$ |
| | 1426 | $\delta_{\text{as}}(\text{CH}_3)\text{N, C}$, $\delta_{\text{s}}(\text{CH}_3)\text{N, C}$ | | | |
| 1409 | | $\delta_{\text{s}}(\text{CH}_3)\text{N}$ | 1407 ^a | 1400 | $\delta_{\text{s}}(\text{CH}_3)\text{N}$ |
| 1376 | | $\delta(\text{CH})$ | 1382 | | $\delta(\text{CH})$ |
| | 1377 | $\delta_{\text{s}}(\text{CH}_3)\text{C}$ | | 1352 | $\delta_{\text{s}}(\text{CH}_3)\text{C}$ |
| 1291 } 1270 } | | $w(\text{CH}_3)\text{N?}$ | 1277 } 1263 } | 1273 | $\nu_{\text{as}}(\text{C}'\text{NC}'')$ |
| 1213 } 1201 } 1190 } | 1257 | $\nu(\text{CN}) + \delta(\text{NH})$ | | | |
| ~1152 | 1181 | $w(\text{CH}_3)\text{N}$ | 1150 | 1184 | $w(\text{CH}_3)\text{N}$ |
| | 1100 | $w(\text{CH}_3)\text{C}$ | | 1059 | $w(\text{CH}_3)\text{C}$ |

TABLE I (Continued)

| NMF | NMA | ASSIGNMENT | DMF | DMA | ASSIGNMENT |
|-------------------|------------------|-------------------------------|----------------------|----------------------|-------------------------------|
| 1040 | | $\tau(\text{CH}_3)\text{N}$ | 1091 1082 1074 | 1040 | $\tau(\text{CH}_3)\text{N}$ |
| | 1045 | $\tau(\text{CH}_3)\text{N,C}$ | | 1021 1014 1007 | $\tau(\text{CH}_3)\text{C}$ |
| 1015 ^a | | $\gamma(\text{CH})$ | | | |
| 1010 | | | | | |
| 989 | | $w(\text{CH}_3)\text{N?}$ | | | |
| 961 | | | | | |
| 949 | 971 | $\nu(\text{C}'\text{N})$ | | | |
| 935 | | | | | |
| | 812 | $\nu(\text{CC})$ | | 960 ^a | $\nu(\text{CC})$ |
| 798 | | ? | 875 865 856 | 734 | $\nu_s(\text{C}'\text{NC}'')$ |
| 616 | | | 669 | 598 | |
| 587 | 626 | $\delta(\text{OCN})$ | 659 649 | 590 583 | $\delta(\text{OCN})$ |
| ~500 | | $\gamma(\text{NH})$ | | | |
| | 431 ^a | $\delta(\text{CCO})?$ | | 460 | $\epsilon(\text{CCO})?$ |

^a liquid spectrum

by analogy with NMF and NMA, and the residual bands between 1300 cm^{-1} and 700 cm^{-1} to the antisymmetric and symmetric modes of the $\text{C}'\text{NC}''$ group. The latter would be expected to give rise to strong and weak bands, respectively, in the infrared, with the reverse order of intensity in the Raman. The moderately strong infrared bands at 1270 cm^{-1} and 1273 cm^{-1} are therefore assigned to $\nu_{\text{as}}(\text{C}'\text{NC}'')$ in DMF and DMA. A corresponding displacement was not observed in the Raman spectrum of DMF (14, 15), but a fairly weak line appears at 1258 cm^{-1} in that of DMA (16). Very weak infrared absorptions at 865 cm^{-1} and 734 cm^{-1} in the vapor spectra of DMF and DMA are assigned to the symmetric mode $\nu_s(\text{C}'\text{NC}'')$. A strong line is observed in the Raman spectrum of DMF at 860 cm^{-1} (14, 15), and the line at 733 cm^{-1} is the strongest displacement in the Raman spectrum of DMA (16). The moderately strong absorption at 470 cm^{-1} in the infrared spectrum of DMA, which is absent in that of DMF, is tentatively assigned to the skeletal mode $\delta(\text{CCO})$.

B. STRUCTURAL FEATURES IN THE VAPOR ABSORPTION BANDS

The principal moments of inertia of the molecules were calculated using the bond lengths given by Kimura and Aoki (17), and assuming all interbond angles to be 120° , except in the case of the methyl group where they were assumed to

TABLE II
MOLECULAR MODELS, MOLECULAR PARAMETERS, AND CALCULATED AND OBSERVED PR BRANCH SEPARATIONS FOR
NMF, NMA, DMF, AND DMA

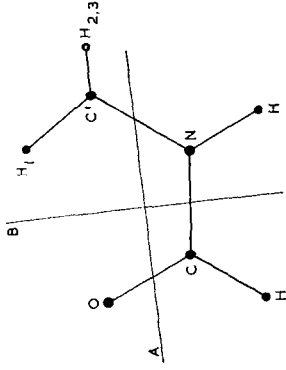
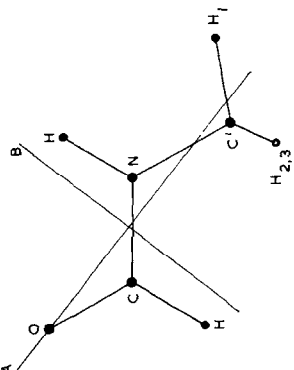
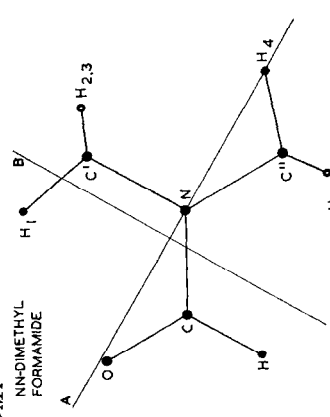
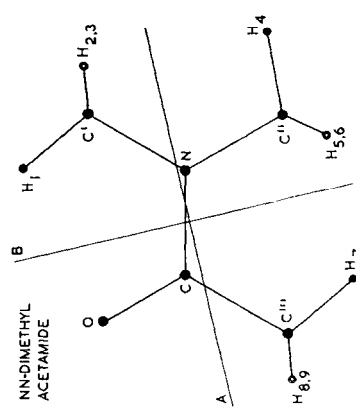
| Molecule | Moments of Inertia ($\times 10^{40}$ g.cm. ²) | | | θ^a | B and Z Parameters (2) | | G and D β Factor (1) | Calculated PR Separations | | Band Type | Observed PR Separations | | | | |
|--|--|----------------|----------------|------------|------------------------|-------------------|----------------------------|---------------------------|--|-----------|-------------------------|----|----|----|----|
| | I _A | I _B | I _C | | ρ | S | | Band Type | PR sep. ⁿ (cm ⁻¹) | | 21 | 21 | 23 | 23 | 26 |
| <p><i>NMF (trans)</i></p> <p>N-METHYLFORMAMIDE-TRANS</p>  | 44 | 125 | 164 | -6° | 2.0 ₈ | -0.7 ₁ | — | A | 25 | PR | 21 | 21 | | | |
| <p><i>NMF (cis)</i></p> <p>N-METHYLFORMAMIDE-CIS</p>  | 21 | 183 | 199 | +37° | 7.8 ₆ | -0.9 ₈ | 8.4 ₈ | Parallel | 21 | PQR | 26 | 27 | 23 | 23 | 26 |

TABLE II—Continued

| Molecule | Moments of Inertia ($\times 10^{40}$ g-cm ²) | | | θ^a | | B and Z Parameters (2) | | G and D β Factor (1) | Calculated PR Separations | | Band Type | Observed PR Separations | | | |
|--|---|----------------|----------------|------------|------------------|------------------------|---|----------------------------|---------------------------|--|-----------|-------------------------|----|----|----|
| | I _A | I _B | I _C | | | ρ | S | | Band Type | PR sep. ^a (cm ⁻¹) | | 14 | 17 | 19 | 20 |
| DMF NN-DIMETHYL FORMAMIDE  | 94 | 191 | 274 | +30° | 1.3 _i | -0.5 _o | — | — | A | 19 | PR | 14 | 17 | 19 | 20 |
| DMA NN-DIMETHYL ACETAMIDE  | 170 | 239 | 393 | -13° | 0.8 _o | -0.0 _z | — | — | A | 16 | PQR | 14 | 15 | | |
| | | | | | | | | | C | 27 | | | | | |

^a Angle between A axis and C—N bond. (+ indicates clockwise rotation).

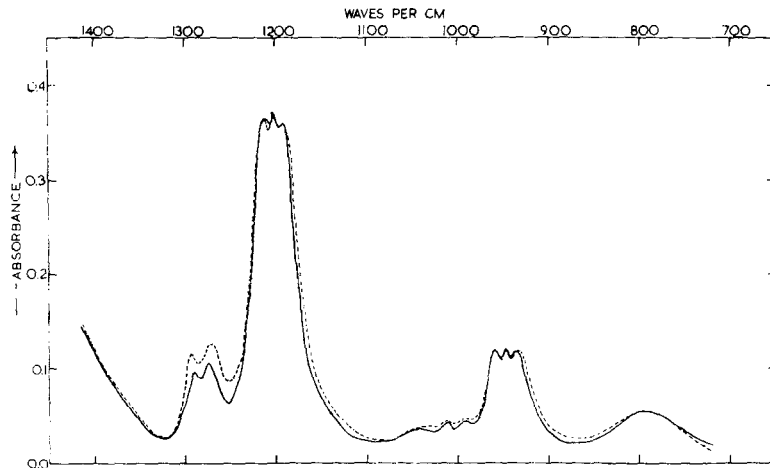


FIG. 2. The vapor spectrum of *N*-methylformamide: — cell temperature 135.5°C, --- cell temperature 198°C. Vapor pressure ~ 90 mm Hg.

be tetrahedral. The relative dispositions of the methyl hydrogen atoms with respect to the molecular skeleton were estimated by a qualitative examination of the Courtauld models, taking into account the repulsion between the *N*-methyl, and formyl and acetyl hydrogens, and the attraction of the acetyl and *N*-methyl hydrogens to the carbonyl oxygen. The moments of inertia, the angles between the *A* axis and the C—N bond, the Badger and Zumwalt parameters *S* and ρ (2), and the calculated and observed PR separations are given in Table II.

(1) *N*-methylformamide

The majority of the band contours in the vapor spectrum of NMF are "parallel-type" with weak central *Q* branches, or "perpendicular-type," featureless bands without a well-defined central maximum. This suggests that the molecule is in the *cis* form, i.e., a symmetric prolate top with the four heavy atoms lying close to the axis of least moment of inertia (6).

Interpretation of the vapor spectrum of NMF in terms of the *cis* configuration alone has been criticized by Miyazawa (18) who suggests that both the *cis* and *trans* forms exist in the vapor phase, that the 1280-cm^{-1} absorption arises from the *cis* form, and those at 1201 cm^{-1} and 949 cm^{-1} from the *trans*. When the vapor spectrum was recorded at 135.5°C and 198°C (Fig. 2) with a continuous stream of vapor passing through the cell, a slight increase in intensity was observed in the band at 1280 cm^{-1} at the higher temperature, and possibly in the very weak band at 1000 cm^{-1} . Both these vapor bands appear here as doublets¹

¹ The band at 1280 cm^{-1} , under the high resolution of a grating instrument, shows an asymmetric contour similar to that in Figs. 1 and 2, but with a weak central *Q* branch (Dr. J. C. Evans, personal communication, 1961).

with a *PR* separation of 21 cm^{-1} , and occur where there is an apparent increase in relative intensity of absorption in the transition liquid \rightarrow dilute solution \rightarrow vapor. Simultaneously, the absorption at 1150 cm^{-1} diminishes in intensity, and almost disappears in the vapor phase. This latter absorption lies close to the mean value (1140 cm^{-1}) of the doublets at 1280 cm^{-1} and 1000 cm^{-1} . In the vapor spectrum at the higher temperature, no corresponding decrease in intensity occurs in the bands at 1201 cm^{-1} , 949 cm^{-1} , or 798 cm^{-1} , which indicates that within the experimental limits set by the short path-length cell and the low vapor pressure of the amide, only one configuration exists in the vapor over this temperature range.

(2) *N-methylacetamide*

One absorption band with well-defined structure is observed in the vapor spectrum of NMA. This is the carbonyl-stretching band at $1731\text{--}1713\text{ cm}^{-1}$, which appears as a *B*-type doublet. The absence of further structural detail does not allow differentiation between the *cis* and *trans* configurations for the molecule; furthermore, the calculated ρ and S values are too close to one another to justify the use of the band contours and *PR* branch separations as a basis for distinguishing between the two proposed molecular models.

(3) *Dimethylformamide*

Badger and Zumwalt (2) show calculated contours for $\rho = 1.25$ and $S = -0.5$ which are close to the corresponding values ($\rho = 1.3_4$ and $S = -0.5_5$) for DMF. The theoretical contours indicate that (i) *A*-type bands have *P*, *Q*, and *R* branches of similar intensity, (ii) *B*-type bands have a doublet structure, and (iii) *C*-type bands have a sharp, intense, central *Q*-branch flanked by fairly well-defined *P* and *R* branches. In the $3\text{--}4\mu$ spectrum of DMF overlapping absorptions render impossible the designation of individual band contours. Beyond 7μ some well-defined contours are observed. The doublet structure of the band at 1270 cm^{-1} is consistent with its assignment to the antisymmetric mode $\nu_{as}(\text{C}'\text{NC}'')$. The contour of the band with a sharp, intense *Q*-branch at 1082 cm^{-1} is consistent with its assignment to a rocking mode of a methyl group attached to nitrogen, and shows the expected increase in *Q*-branch intensity compared with the featureless band observed for the analogous mode in NMF. The *C*-character shown by the in-plane skeletal modes $\nu_s(\text{C}'\text{NC}'')$ and $\delta(\text{OCN})$ at 865 cm^{-1} and 659 cm^{-1} , respectively, is anomalous, but it has been observed that *Q*-branch intensity is not, by itself, an adequate criterion for distinguishing between *A*- and *C*-type contours in asymmetric molecules (19).

(4) *Dimethylacetamide*

An examination of the calculated contours for $\rho = 0.75$ and $S = 0.0$ (2) shows that *A*-type contours for DMA ($\rho = 0.8_0$, $S = -0.0_2$) should be similar

to those for DMF, the *B*-type doublet separation should be smaller, and that the *P* and *R* branches in *C*-type contours should be less well-defined than in the case of DMF. In the observed vapor spectrum of DMA, the contour of the band assigned to the rocking mode of the methyl group attached to carbon has a sharp *Q*-branch with ill-defined *P* and *R* branches as expected on the basis of the theoretical contours. The skeletal mode $\delta(\text{OCN})$ shows an *A*-type absorption with *P*, *Q*, and *R* branches approaching equal intensity, in conformity with the calculated contours.

It is concluded therefore that in the case of molecules with a limited range of asymmetry, the shapes of the absorption bands, and the corresponding *PR* branch separations (Table II, columns 10 and 12) are only in very qualitative agreement with the calculated contours, and that contours observed experimentally under low resolution may only be used to distinguish between configurational isomers which differ appreciably in symmetry.

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