

# Near-Infrared Studies. Norbornenes and Related Compounds<sup>1</sup>

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The identification of norbornenes, norbornadienes, nortricyclanes, and quadricyclanes by near-infrared spectroscopy has been investigated. Absorptions due to the first overtone of the C-H stretching vibration in the 1.645- to 1.675- $\mu$  region have been correlated with skeletal structure, degree of substitution, and the electronic and stereochemical effects of substituents. In general the following correlations have been found: norbornenes, 1.644-1.673  $\mu$  ( $\epsilon$  0.214-0.414 per olefinic C-H); nortricyclanes, 1.656-1.671  $\mu$  ( $\epsilon$  0.240-0.417 per cyclopropyl C-H); and quadricyclanes, 1.652-1.667  $\mu$  ( $\epsilon$  0.319-0.412 per cyclopropyl C-H).

In spite of the many modern analytical techniques available, the organic chemist is often perplexed by the difficult problem of identifying the basic structures of complex molecules. This is particularly true in the case of rigid strained ring systems where the skeletal structures often defy independent synthesis and yield only complex spectrometric data.

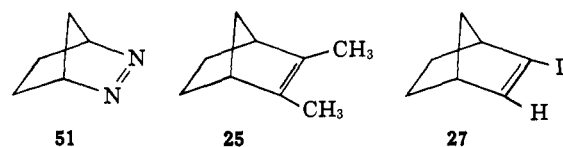
The present investigation is concerned with the use of near-infrared spectroscopy in the identification of derivatives of bicyclo[2.2.1]hept-2-ene and related systems. The several reviews<sup>3-7</sup> which have appeared on near-infrared spectroscopy indicate by their contents the paucity of research which has been carried out in an effort to utilize the near-infrared region of the spectrum to its full capacity.

In connection with our general interest in strained ring systems we have studied the specific absorptions of norbornene and related compounds in the near-infrared region of the spectrum between 1.640 and 1.675  $\mu$  (6098-5970  $\text{cm}^{-1}$ ). Our investigation has disclosed that certain bi-, tri- and quadricyclic ring systems can be positively identified by their unique absorptions of near-infrared energy.

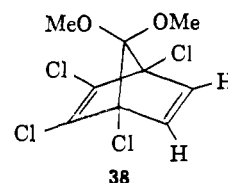
## Results and Discussion

The characteristic absorptions of norbornenes substituted at C-5, C-6 or C-7 are listed in Tables I and II. For convenience the tables have been arranged in the order of increasing energy of the observed absorption. It is well recognized that the region of the spectrum under consideration in this investigation covers an

energy range in which the first overtone of the fundamental C-H stretching vibration occurs.<sup>6</sup> However, it was not immediately obvious which C-H stretching overtone was being measured in our studies. Examination of the compounds listed in Tables I and II (compounds **1** through **24**) indicated that the characteristic overtone band was due either to the C-H stretch of the vinyl hydrogens or to the C-H stretch of the bridgehead hydrogens at C-1 and C-4. The possibility that the observed absorption might have been due to the hydrogens at C-5, C-6, or C-7 was ruled out because the characteristic absorption continued to appear when these positions were substituted with other groups. One indication that the observed overtone band was due to the C-H stretch of the vinyl hydrogens was the finding that 2,3-diazonorbornene (**51**) showed no absorption in the 1.600- to 1.685- $\mu$  region. Definitive evidence that the characteristic



absorption was due to the first overtone of the C-H stretching vibration of the vinyl hydrogens was obtained from a measurement of the spectra of santene (**25**) and 2-deuterionorbornene (**27**). Santene showed no absorption of energy in the near-infrared region of the spectrum below 1.700  $\mu$ . 2-Deuterionorbornene gave a peak at 1.664  $\mu$  with *ca.* half the molar absorptivity of a norbornene with two vinyl hydrogens. Approaching the problem from a different direction we synthesized **38** which possessed substituents other than hydrogen at both C-1 and C-4. The absence of these



bridgehead hydrogens had no effect on the occurrence of the characteristic norbornene absorption. Thus the typical near-infrared maximum which norbornenes have in the 1.644- to 1.673- $\mu$  region must be attributed to the first overtone of the fundamental C-H stretching vibration of the vinyl hydrogens.

The exact position of the absorption peak of a substituted norbornene is closely related to two factors: the electron inducing properties of substituents on the bicyclic system and the presence of electron-rich groups in close spatial proximity to the double bond. For lack of better terminology the latter effect will hereafter be referred to as an "electrostatic field effect."

(1) Presented in part before the Division of Organic Chemistry, 141st National Meeting of The American Chemical Society, Washington, D. C., March 1962, Abstracts, p. 27-O.

(2) Based in part upon the M.S. Dissertation submitted by W. M. Hooker, The Ohio State University, 1963.

(3) W. I. Kaye, *Spectrochim. Acta*, **6**, 257 (1954).

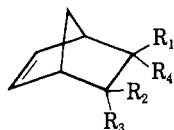
(4) O. W. Wheeler, *Chem. Rev.*, **59**, 629 (1959).

(5) W. I. Kaye, "The Encyclopedia of Spectroscopy," G. L. Clark, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 494.

(6) R. F. Goddu, "Advances in Analytical Chemistry and Instrumentation," C. N. Reilly, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 347.

(7) D. L. Nealy, Massachusetts Institute of Technology Seminar in Organic Chemistry, fall, 1963, p. 346.

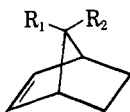
**Table I.** Near-Infrared Maxima of Norbornenes Substituted in the 5- and/or 6- Positions



No.	Substituent				Absorption peak		
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	$\mu$	Cm. <sup>-1</sup> <sup>a</sup>	Molar absorptivity
1	H	H	H	H	1.663	6013	0.428
2	H	H	CH <sub>3</sub>	CH <sub>3</sub>	1.663	6013	0.612
3	CH <sub>3</sub>	H	CH <sub>3</sub>	H	1.662	6017	0.532
4	H	H	CH <sub>2</sub> OH	CH <sub>2</sub> OH	1.662	6017	0.492
5	CH <sub>2</sub> OH	H	CH <sub>2</sub> OH	H	1.661	6020	0.576
6	H	H	CH=CH-CH <sub>2</sub>		1.661	6020	0.654
7	H	H	OH	H	1.660	6024	0.478
8	H	CH <sub>2</sub>		H	1.659	6028	0.595
9	CH <sub>2</sub> OH	CH <sub>2</sub> OH	H	H	1.659	6028	0.634
10	CO <sub>2</sub> Me	CO <sub>2</sub> Me	H	H	1.659	6028	0.704
11	H	H	H	CO <sub>2</sub> H	1.658	6031	0.558
12	H	H	H	C≡N	1.656	6039	0.468
13	C≡N	H	H	H	1.654	6046	0.464
14			H	H	1.654	6046	0.608
15	H			H	1.654	6046	0.558
16	H	H			1.653	6050	0.620
17	COCl	H	COCl	H	1.653	6050	0.566
18	Cl	H			1.652	6053	0.688
19	H	H	CO <sub>2</sub> Me	CO <sub>2</sub> Me	1.647	6072	0.514

<sup>a</sup> The wave numbers listed in all tables are accurate to  $\pm 2$  cm.<sup>-1</sup>.

**Table II.** Near-Infrared Maxima of Norbornenes Substituted in the 7-Position



No.	Substituent		Absorption peak		
	R <sub>1</sub>	R <sub>2</sub>	$\mu$	Cm. <sup>-1</sup>	Molar absorptivity
1	H	H	1.663	6013	0.428
20	H	OH	1.660	6024	0.442
21	CH <sub>2</sub>		1.660	6024	0.585
22	OMe	OMe	1.659	6028	0.494
23			1.657	6035	0.822
24			1.656	6039	0.624

Table I clearly illustrates the trend for a shift to shorter wave length with an increase in the strength and number of the electron withdrawing groups. In general there is an almost linear relationship between the energy of the C-H stretching vibration and the electron withdrawing properties of the substituents on compounds 1 through 18 in Table I and compounds 20 through 24 in Table II. Compound 19 is a special case which will be discussed in a following section.

The correlation of substituent constants of functional groups with infrared group frequencies has been of considerable interest in recent years.<sup>8</sup> In the ali-

phatic series the carbonyl stretch of ketones<sup>9</sup> and amides<sup>10</sup> has been studied as a function of substituent constants. In addition, the OH stretch of acids,<sup>11</sup> the asymmetric nitro stretch,<sup>12</sup> and the nitrile stretching frequency<sup>13</sup> have been correlated with the Taft  $\sigma^*$ -constants of substituent groups. A correlation of the first overtone of the cyclopropyl C-H stretching vibration with the substituent constants of functional groups has also been obtained.<sup>14</sup> Thus, the systematic shift in wave length of the olefinic C-H stretch in norbornenes with the change in the electron withdrawing properties of the substituents was not unusual. However, the number of carbon atoms through which this inductive effect was active does merit special notice.

As stated earlier in this discussion, compound 19 was distinctly out of place on the basis of inductive effects. Whereas 10 has the same functional groups as 19, the position of the characteristic near-infrared absorption peaks of 10 and 19 differed greatly. Since the inductive effect of the two carbomethoxy groups should not differ with stereochemistry, the drastic shift in the absorption frequency must be due to some

R. Venkataraghavan, *Can. J. Chem.*, **39**, 1757 (1961); see also L. J. Bellamy, *J. Chem. Soc.*, 4221 (1955).

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(10) T. L. Brown, J. F. Regan, R. D. Schultz, and J. C. Steenberg, *J. Phys. Chem.*, **63**, 1324 (1959).

(11) J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

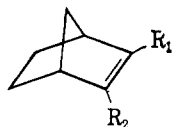
(12) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); J. Mason and J. Dunderdale, *ibid.*, 759 (1956).

(13) J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958).

(14) P. G. Gassman, *Chem. Ind. (London)*, 740 (1962).

(8) For a discussion of these correlations see C. N. R. Rao and

**Table III.** Near-Infrared Maxima of Norbornenes Substituted in the 2-Position

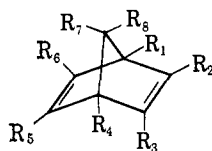


No.	Substituent		Absorption peak		Molar absorptivity/vinyl hydrogen
	R <sub>1</sub>	R <sub>2</sub>	$\mu$	Cm. <sup>-1</sup>	
25	CH <sub>3</sub>	CH <sub>3</sub>	No peak below 1.700 $\mu$		
26	H	CH <sub>3</sub>	1.673	5977	0.262
27	H	D	1.664	6010	0.294
1	H	H	1.663	6013	0.214
28	H	CO <sub>2</sub> CH <sub>3</sub>	1.657	6035	0.455
29	H	CO <sub>2</sub> H	1.656	6039	0.526
30	H	Cl	1.653	6050	0.381
31	H	Br	1.653	6050	0.414

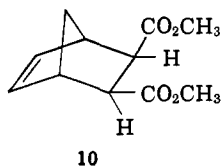
norbornene derivative we have the nonbonding electrons on nitrogen readily available for a spatial interaction with the double bond. A similar shift to shorter wave length appears prevalent for all the norbornadienes listed in Table IV. In the case of the norbornadienes there are  $\pi$ -electrons on both sides of the bicyclic system which can interact with the  $\pi$ -electron clouds across the rings. Again this shift could be attributed to an "electrostatic field effect." Unfortunately in the case of the norbornadienes it cannot be demonstrated whether this shift to shorter wave length is not merely a result of the strain incorporated into the bicyclic system by the addition of a second double bond or to the inductive effect of one double bond on the other.

Tables III and IV list norbornenes and norbornadienes with substituents in some of the vinylic positions. The compounds in Table III represent a series where the

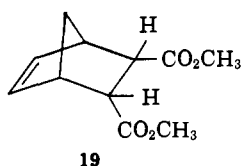
**Table IV.** Near-Infrared Maxima of Norbornadienes



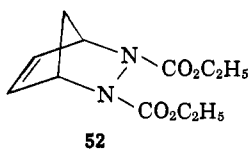
No.	Substituent								Absorption peak		Molar absorptivity/vinyl hydrogen
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	$\mu$	Cm. <sup>-1</sup>	
32	H	H	H	H	H	H	H	H	1.655	6042	0.317
33	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	1.655	6042	0.338
34	H	H	H	H	H	H	OH	H	1.654	6046	0.335
35	H	CO <sub>2</sub> H	H	H	H	H	H	H	1.651	6057	0.413
36	H	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	H	H	H	H	H	1.649	6064	0.359
37	H	C $\equiv$ N	C $\equiv$ N	H	H	H	H	H	1.646	6075	0.412
38	Cl	Cl	Cl	Cl	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	1.644	6083	0.597



10



19



52

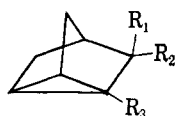
other effect. We feel that this effect is an "electrostatic field effect" arising from the spatial proximity of the carbonyl groups of one of the esters to the  $\pi$ -electrons of the carbon-carbon double bond.<sup>15</sup> Since the two carbonyl groups would repel each other, one would be expected to be jutting out from the bicyclic system with the *o*-methyl group toward the double bond, while the second carbonyl would be close to the olefinic group with its *o*-methyl group pointing away. Additional evidence for this type of noninductive electronic effect was observed in the case of 5,6-dicarboethoxy-5,6-diazabicyclo[2.2.1]hept-2-ene (52). Compound 52 had  $\lambda_{\text{max}}$  1.649  $\mu$ . This is close to the value of 1.647  $\mu$  observed for 19. In the 5,6-diaza-

functional groups have replaced one of the vinyl hydrogens. In general, the peak positions were as anticipated on the basis of inductive effects, the inductive effect being much greater when the functional group is bonded directly to the double bond. The fact that some of these groups possessed a carbonyl in conjugation with the double bond seemed to have little effect on the position of the absorption peak. The intensity of the absorption was greatly influenced by the presence of a conjugating group in the vinylic position. Compounds 28 and 29 clearly illustrate this principle since their molar absorptivity was approximately twice as large as the anticipated values. The mesomeric effects of the chlorine in 30 and the bromine in 31 appear to parallel the situation observed with 28 and 29. Again the peak position was nicely correlated with the inductive nature of the halogen and the molar absorptivity was enhanced.

The norbornadienes listed in Table IV all show a shift to a shorter wave length than that observed for the analogously substituted norbornenes. Whereas norbornene (1) had a peak at 1.663  $\mu$ , norbornadiene (32) had its absorption maximum at 1.655  $\mu$ . In general,

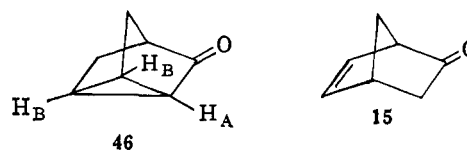
(15) An analogous situation has been discussed for  $\alpha$ -haloketones by L. J. Bellamy, L. C. Thomas, and R. L. Williams, *J. Chem. Soc.*, 3704 (1956).

Table V. Near-Infrared Maxima of Nortricyclanes



No.	Substituent			Absorption peak		Molar absorptivity/ cyclopropyl hydrogen
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	$\mu$	Cm. <sup>-1</sup>	
39	CH <sub>3</sub>	H	CH <sub>3</sub>	1.671	5984	0.240
40	CH <sub>3</sub>	CH <sub>3</sub>	H	1.667	5998	0.267
41	H	H	H	1.664	6010	0.408
42	OH	H	H	1.663	6013	0.417
43		H	H	1.660	6024	0.387
44		H	H	1.660	6024	0.410
45	Br	H	H	1.659	6028	0.387
46		H	H	1.659 <sup>a</sup>	6028	0.333 <sup>a</sup>
47	H	H	CO <sub>2</sub> H	1.656	6039	0.576
46		H	H	1.649 <sup>a</sup>	6064	0.253 <sup>a</sup>

<sup>a</sup> Nortricyclanone exhibits two overlapping peaks. Owing to the overlap of these peaks the observed maxima and molar absorptivities are probably a composite of the C-R<sub>3</sub> stretching overtone and the other two identical cyclopropyl C-H stretching overtones.

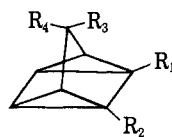


ing vibration of C-H<sub>A</sub> while the peak at 1.659  $\mu$  was associated with the C-H<sub>B</sub> energy absorption. By comparison dehydronorcamphor (15) had a single peak at 1.654  $\mu$ , a wave length midway between the two absorption peaks of nortricyclanone.

The near-infrared maxima observed for quadricyclanes (Table VI) were closely related to nortricyclanes in the wave length of the energy absorbed. In the three examples which were investigated the peak position was shortened by electron withdrawing groups and the molar absorptivity per cyclopropyl hydrogen was approximately the same as the molar absorptivity per cyclopropyl hydrogen in the nortricyclanes.

The differentiation of norbornenes, norbornadienes, nortricyclanes, and quadricyclanes by near-infrared spectroscopy is relatively simple. This is illustrated by the spectra shown below and by the data tabulated in Table VII. Although norbornadiene seems very

Table VI. Near-Infrared Maxima of Quadricyclanes



No.	Substituent				Absorption peak		Molar absorptivity/ cyclopropyl hydrogen
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	$\mu$	Cm. <sup>-1</sup>	
48	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	1.667	5998	0.397
49	H	H	H	H	1.661	6020	0.319
50	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	H	H	1.652	6053	0.412

there is a change of 0.008  $\mu$  in going from a 5,6-disubstituted norbornene to the analogously substituted norbornadiene. The norbornadienes also have an enhanced molar absorptivity per olefinic hydrogen when compared with the norbornenes.

Table V lists the assorted nortricyclane derivatives which have been studied. Curiously, the characteristic nortricyclane maxima were almost identical in peak position with the analogously substituted norbornenes. Although norbornene (1) and nortricyclane (41) could not be easily distinguished from one another by their peak positions (1.663 and 1.664  $\mu$ , respectively), they were easily differentiated by their molar absorptivity which was 0.428 for 1 and 1.224 for 41. The similarly substituted norbornenes and nortricyclanes gave analogous results insofar as the wave length of the absorptions were nearly the same while the peak intensities for the nortricyclanes were usually twice as large as the peak intensities for the norbornenes. In this regard nortricyclanone (46) represents a unique situation since it is the only compound studied which gave more than one absorption peak in the region being studied. The absorption at 1.649  $\mu$  was attributed to the stretch-

Table VII. Comparison of Related Systems

Compd.	No.	Absorption peak, $\mu$	Molar absorptivity	Molar absorptivity/absorbing hydrogen
	1	1.663	0.428	0.214
	32	1.655	1.268	0.317
	41	1.664	1.224	0.408
	49	1.661	1.914	0.319

similar to nortricyclane, the salient shortening of the peak wave length in norbornadiene permits facile identification.<sup>16-18</sup>

(16) In addition the presence of the double bonds in the norborna-

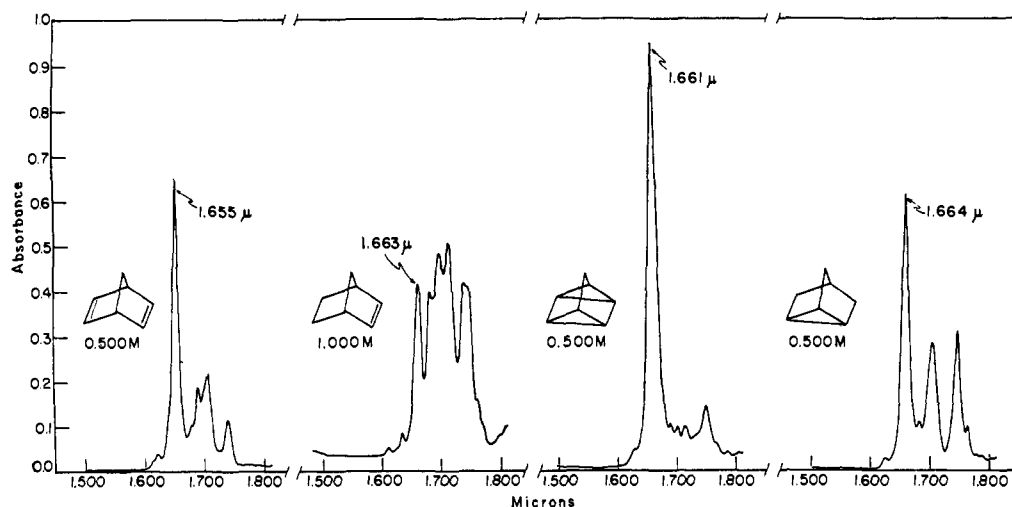


Figure 1. Typical near-infrared spectra of norbornene and related compounds in carbon tetrachloride solution.

There are certain interfering factors which merit discussion in relation to the identification of norbornenes and related systems by near-infrared spectroscopy. The principle problem is sample size, the minimum amount of sample being in the order of 0.5 mmole. Secondly, the compound under investigation must be soluble, at least to the extent of 0.05 mole/l., in a proton-free solvent such as carbon tetrachloride. Finally the compound being studied must be free of aromatic compounds which tend to have absorption peaks in the same region of the spectrum.

#### Experimental

*Near-Infrared Spectral Procedures.* Near-infrared spectra were measured on an Applied Physics Corp. Cary Model 14 recording spectrophotometer. The instrument was calibrated using didymium glass and polystyrene. Slit width was automatically controlled at 0.15 mm. at 2.000  $\mu$  (see Figure 1).

Carbon tetrachloride was used as the solvent in all cases. Most of the compounds studied were at a concentration of either 0.500 or 1.000 *M*. These measurements were made using 1-cm. matched silica

dienes can be easily detected either by chemical means or by other spectroscopic methods.

(17) Compounds 28 and 29 were not included in this table because they represent exceptions to the rule due to the greatly enhanced molar absorptivity resulting from conjugation of the carbonyl with the double bond.

(18) Compound 38 represents an exception to the rule. The molar absorptivity (0.597 per vinyl hydrogen) was unusually large. This was probably due to the polychlorinated nature of the molecule.

cells. Compounds 9, 14, 16, and 17 were 0.025 *M* solutions, 11 was 0.050, and 18 was 0.100 *M* due to solubility problems. These solutions were measured in 10-cm. silica cells. Molar absorptivities were reproducible when the concentrations were varied by a factor of ten. Wave length precision in the region 1.600 to 1.700  $\mu$  was of the order  $\pm 0.0005 \mu$ .

*Sources of Compounds.* Compounds 1 and 6 were obtained from commercial sources and were purified before use. Compounds 28, 29, 41, 43, 44, 45, and 47 were supplied by Dr. R. Finnegan. Compounds 2, 3, 4, 5, 9, 10, 14, 17, and 19 were donated by Drs. K. Greenlee and B. Otto. Dr. N. LeBel supplied 30 which was also used as the starting material for the preparation of 27. Nortricyclanol (42) and nortricyclanone (46) were given to us by Dr. J. Meinwald. Compounds 12 and 13 were furnished by Dr. R. Ouellette. Compounds 26 and 31 were obtained from Dr. P. Schleyer. The other 27 compounds were synthesized in this laboratory. All compounds investigated were better than 98% pure with the exception of 2-deuterionorbornene (27) which was contaminated with 15% norbornene. The molar absorptivity listed for 27 was that calculated for pure 2-deuterionorbornene.

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