Intercalates of Vanadyl Phosphate with Benzonitrile and Tolunitrile

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Intercalates of vanadyl phosphate with benzonitrile and *p*-tolunitrile were prepared and characterized by X-ray powder diffraction, TG analysis, IR and Raman spectroscopy. Both intercalates contain one nitrile molecule per formula unit. The intercalates prepared are moisture sensitive and guest molecules are easily replaced by water molecules. The nitrile molecules are anchored to the host layers by an N–V donor-acceptor bond. Local structures and interactions appearing in the intercalates were suggested on the base of quantum chemical calculations. These calculations support the results of the IR and Raman spectroscopy, indicating the formation of a C≡N→V bond in the intercalates. The calculated basal spacings (11.32 Å for the benzonitrile and 13.00 Å for the tolunitrile intercalates) are in good agreement with the experimental values (11.22 and 13.19 Å, respectively).

Introduction

Vanadyl phosphate is able to accommodate various types of organic compounds having Lewis base character.[1] Less attention has been paid to intercalations of carboxylic acids[2] and their derivatives.[3−6] Intercalates of vanadyl phosphate with nitriles (acetonitrile, propionitrile, butyronitrile, valeronitrile, hexanenitrile)[5] and dinitriles (malononitrile, succinonitrile, glutaronitrile, adiponitrile, pimelonitrile, suberonitrile)[6] were prepared. The nitrile intercalates (except for acetonitrile) contain one nitrile molecule per formula unit. The dinitrile content in the intercalates decreases with increasing chain length. In contrast to most $VOPO_4$ intercalates with guest molecules containing aliphatic chains where the basal spacing increases with increasing chain length,[2,7−11] the basal spacings of all the nitrile and the dinitrile intercalates prepared are practically the same. This demonstrates that the aliphatic part of the guest molecules must be parallel to the host layers.

In this paper we report on the intercalation of benzonitrile and *p*-tolunitrile into vanadyl phosphate to complete the picture on the intercalation ability of vanadyl phosphate towards different nitriles.

Results and Discussion

Similarly to aliphatic nitriles and dinitriles, the aromatic nitriles analysed cannot be intercalated directly into anhydrous vanadyl phosphate and also a replacement of the water molecules in $VOPO_4 \cdot 2H_2O$ does not lead to an intercalation. The benzonitrile and *p*-tolunitrile intercalates can be prepared by replacing 2-propanol or 1-propanol in the corresponding $VOPO_4$ intercalates. While the 2-propanol molecules are replaced very easily, the replacement of the 1-propanol molecules is very slow and intermediate phases are formed. Therefore, it is necessary to repeat the reaction with a new amount of the corresponding nitrile.

The intercalates prepared are greenish-yellow crystalline solids, indicating that only a small part of vanadium(V) has been reduced to vanadium(IV). The diffractogram of the benzonitrile intercalate shows sharp (00*l*) and weak (200 and 201) reflections (Figure 1a). Reflections at 201, 202 and 310 are present in the diffractogram of the *p*-tolunitrile intercalate (Figure 1b). The low intensity of a few (*hkl*) lines in the intercalates suggests a turbostratic structure where the original tetragonal layers of the host are retained, but are shifted in the directions of the *x* and/or *y* axes. The lattice parameters of the tetragonal structures are $a = 6.21$ Å, $c = 11.22$ Å and $a = 6.21$ Å, $c = 13.19$ Å for the benzonitrile and tolunitrile intercalates, respectively.

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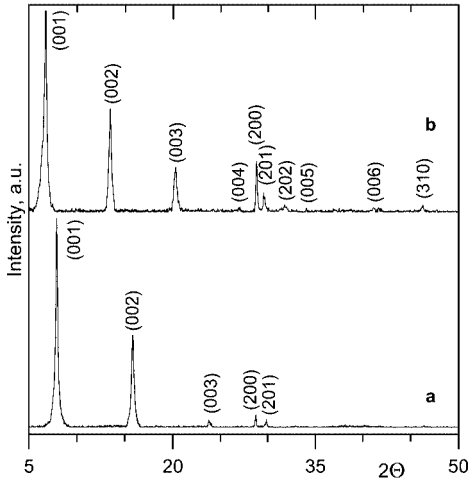

Figure 1. Diffractogram of benzonitrile (a) and *p*-tolunitrile (b) intercalated $VOPO_4$

The compositions of the intercalates were determined by thermogravimetric analysis (see Figure 2). During heating, nitriles are slowly released in two steps in the temperature range 100−550 °C. The second step is very slow and the DTA shows a broad exothermic peak probably due to the combustion of the nitriles. The product of the thermal decomposition is anhydrous vanadyl phosphate. Total weight losses correspond to the stoichiometric ratio $x = 1$, that is, one molecule of nitrile per formula unit (for the benzonitrile intercalate: calcd. 38.9%; found 38.1% and for the *p*-tolunitrile intercalate: calcd. 42.2%; found 40.9%).

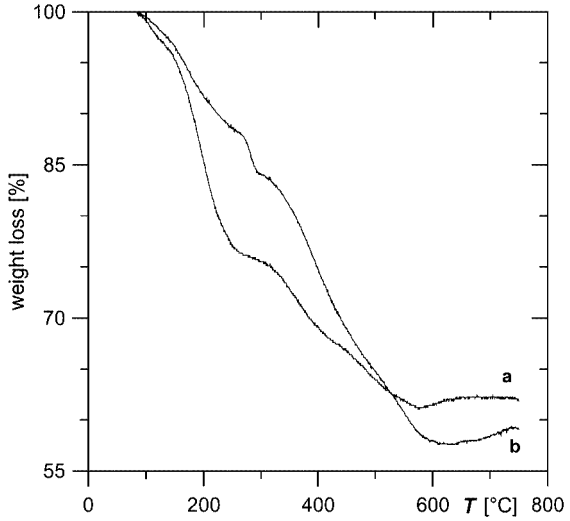

Figure 2. TG curves of the benzonitrile (a) and *p*-tolunitrile (b) intercalates

The benzonitrile and *p*-tolunitrile intercalates are more stable in air (at relative humidity 40−50%) than the nitrile intercalates[5] and less stable than the dinitrile intercalates.[6] The course of the hydration of both intercalates was followed by XRD. A small amount of dihydrate appeared after twenty minutes and the intercalates were completely decomposed after one day.

The character of the bonding between the guest and the host layers in the nitrile intercalates was studied by IR and Raman spectroscopy. From the point of view of the host-guest interaction, the most important position is that of the C≡N stretching vibration. The C≡N group can act either as a σ-donor, by donating nitrogen electrons to a metal, or as a π-donor, by donating electrons of a nitrile π-bond. The wavenumber of the C≡N stretching vibration is shifted to higher values in the case of σ-donation and to lower values in the case of π-donation.[12]

The IR spectra of pure benzonitrile and its $VOPO_4$ intercalate (KBr pellet and Nujol suspension), in the region from 2100 to 2400 cm^{-1}, are given in Figure 3. The strong C≡N stretching absorption band of pure benzonitrile is observed at 2228 cm^{-1}. In the spectrum of the benzonitrile intercalate, measured as a Nujol suspension, we observed two absorption bands at 2228 and at 2252 cm^{-1}. No shifted nitrile band was observed in the samples prepared as KBr pellets. The band with the same position as in the pure benzonitrile spectrum most probably corresponds to free benzonitrile molecules, which are present in the sample due to the instability of the intercalate in air. While preparing the KBr pellets the samples decomposed to free nitrile and vanadyl phosphate hydrate. In the case of the Nujol dispersion only a partial decomposition takes place. The shifted band observed at 2252 cm^{-1} in the IR spectrum of the Nujol suspension corresponds to coordinated benzonitrile. The observed shift indicates the formation of a C≡N→V bond in the intercalate.

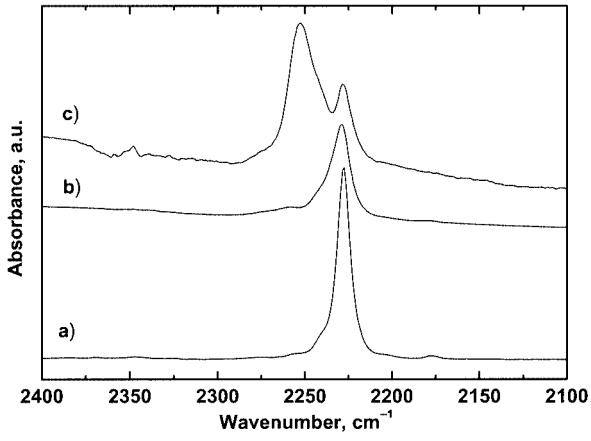

Figure 3. FTIR spectra of pure benzonitrile measured by the ATR technique (a) and of the benzonitrile intercalate measured as a KBr pellet (b) and as a Nujol suspension (c)

The Raman spectra of benzonitrile and its intercalate in the region from 400 to 4000 cm^{-1} are given in Figure 4. One can observe the intense band of the symmetric $\nu(PO_4)$ stretching vibration of a phosphate tetrahedron in the $(VOPO_4)_\infty$ layers. It is situated at about 941 cm^{-1} in the spectrum of the intercalate. Strong bands of aromatic vibrations at the same positions as in the spectrum of pure benzonitrile (1002, 1600 and 3078 cm^{-1}) are observed in the spectrum of the intercalate. The spectrum of the intercalate confirms that the structure of the original $VOPO_4$ layers

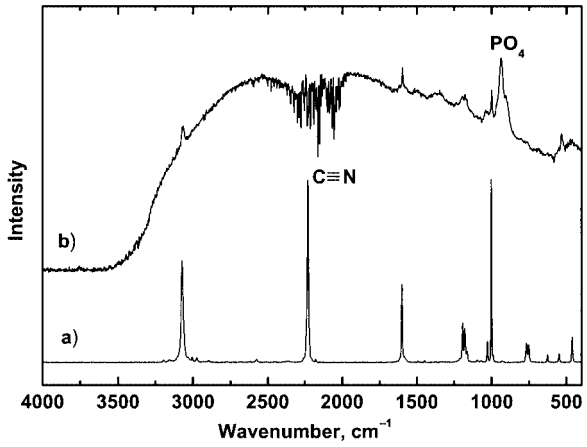

Figure 4. Raman spectra of liquid benzonitrile (a) and the benzonitrile intercalate (b)

remains unchanged and there are no significant changes in the guest molecules after intercalation. The vanadyl stretching band expected at about 1002 cm^{-1}, which appears to be especially sensitive to atoms coordinated to vanadium within an octahedral arrangement in the host-lattice structure, overlaps with one of the benzonitrile bands. The part of the Raman spectrum corresponding to the nitrile stretching vibration is strongly influenced by the baseline radiation. This is most probably due to the excitation of the benzonitrile molecules by the laser beam while the measurements were being performed.

The infrared spectra of pure tolunitrile and its intercalate in $VOPO_4$ (as a KBr pellet and as a Nujol suspension) in the region from 2100 to 2400 cm^{-1} are given in Figure 5. The strong C≡N stretching absorption band of pure tolunitrile is observed at 2228 cm^{-1}, exactly at the same position as for pure benzonitrile. There are three absorption bands at 2228, 2256 and 2269 cm^{-1} in the IR spectrum of the tolunitrile intercalate measured in the Nujol suspension. New shifted bands at 2256 and 2269 cm^{-1} correspond to two non-equivalent tolunitriles. From the fact that only one shifted nitrile band (2269 cm^{-1}) is observed in the IR spectrum of the tolunitrile intercalate dispersed in the KBr pellet, it follows that the bands at 2256 and 2269 cm^{-1} correspond to two (slightly different) arrangements of tolunitrile in the interlayer space.

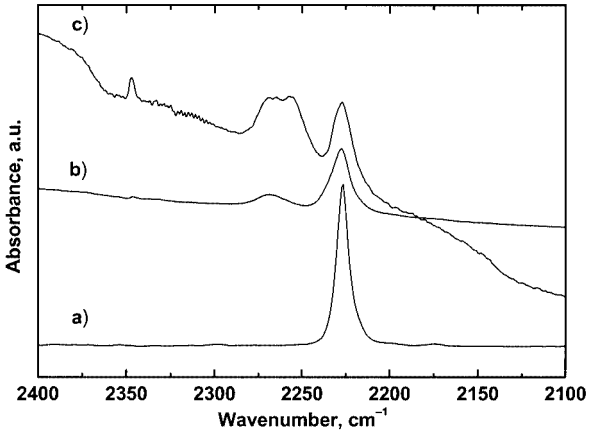

Figure 5. FTIR spectra of pure tolunitrile (a) and the tolunitrile intercalate measured as a KBr pellet (b) and as a Nujol suspension (c)

The Raman spectra of tolunitrile and its intercalate in the region from 400 to 4000 cm^{-1} are given in Figure 6. Only a part of the intercalate spectrum, including an intense band for the symmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron in the $(VOPO_4)_\infty$ layers situated at about 903 cm^{-1}, can be observed. The band for the aromatic vibration of tolunitrile is observed at about 1605 cm^{-1}. The part of the spectrum above 1800 cm^{-1} could not be measured due to the strong influence of the baseline radiation.

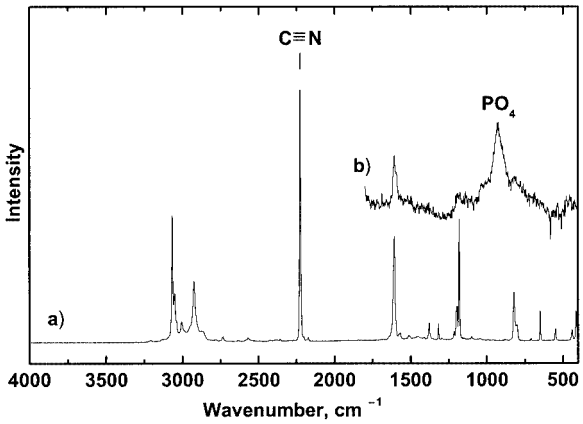

Figure 6. Raman spectra of liquid *p*-tolunitrile (a) and its intercalate (b)

The conclusions on the character of the bonding between the guest and the host layer in the nitrile intercalates are strongly supported by the results of quantum mechanical calculations and modeling. Figure 7 shows a DFT optimized structure of the molecular segment representing interactions of vanadyl phosphate with nitriles. In order to make the electronic structure in the segment close to the conditions appearing in the intercalates, free terminal oxygen atoms were substituted by OH groups and the total charge of the model compound was set to +3, the nitrile group being represented by acetonitrile. It was found that all the geometry optimizations, with various starting orientations for the acetonitrile with respect to the vanadyl group, lead to the structure displayed in Figure 7. Quantum chemical calculations thus support the results of the IR and Raman spectroscopy indicating the formation of the C≡N→V bond in the intercalates.

Because of the size and computational demand, the simulation of larger local intercalate structures, including two $VOPO_4$ layers, could only be done by using the semiempirical quantum-chemical method PM3. However, the model structure shown in Figure 7 was reoptimized with the PM3 method and only slight changes in optimized molecular parameters were found in comparison with a high precision DFT approach. This indicates that no serious artifacts are produced by the semiempirical PM3 method. The optimized geometries of the molecular segments, representing two

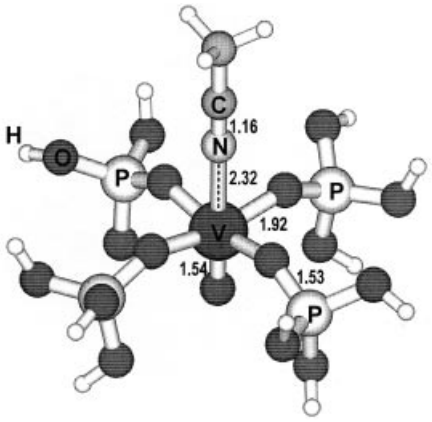

Figure 7. Optimized DFT structure of the molecular segment modeling the vanadyl phosphate-nitrile interaction, with indicated bond lengths (in Å)

layers of $VOPO_4$ and five molecules of benzonitrile and *p*-tolunitrile, intercalated between the two layers, are given in Figures 8 and 9, respectively. Free terminal oxygen atoms were substituted by OH groups and the total charge of the model compounds was set to −2. The coordination of the vanadium atoms to the nitriles in adjacent guest interlayer spaces was simulated by coordinating acetonitrile molecules, which are not shown in Figures 8 and 9. The initial geometrical parameters (bond lengths and angles) for the $VOPO_4$ layers were taken from the experimental X-ray diffraction data determined for $VOPO_4 \cdot 2H_2O$[13] and the initial basal spacings were set to the above given values of the lattice parameters c = 11.22 and 13.19 Å, determined by X-ray diffraction for the benzonitrile and *p*-tolunitrile intercalates, respectively. The first geometrical optimizations of the model structures were performed under various symmetry constraints and fixed parameters c. In the final energy minimization all the variables defining the positions of the atoms, both in the host and guest layers, were fully optimized, with the exception of the constraints arising from the symmetry conditions defining the polyhedra in the $VOPO_4$ layers and the relative orientations of four equivalent guest molecules in the interlayer space with respect to the $VOPO_4$ layer. The calculated basal spacings of 11.32 Å for benzonitrile and 13.00 Å for tolunitrile are in good agreement with the experimental values of 11.22 and 13.19 Å, respectively. The mutual position of the successive layers exhibits a shift that can be characterized by a vector with the components 0.12 and 0.14 Å for the benzonitrile and 0.08 and 0.06 Å for the tolunitrile intercalates.

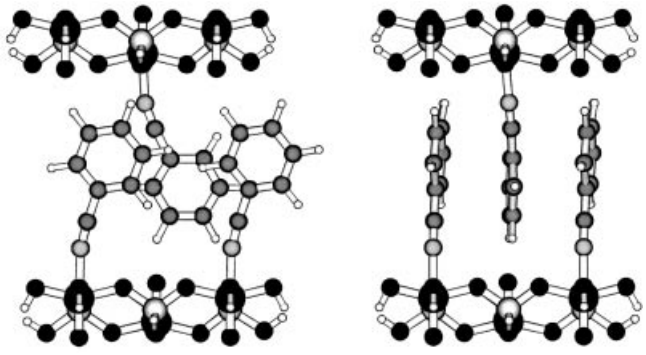

Figure 8. Side view of the PM3 optimized geometry of the molecular segment modeling the arrangement of benzonitrile molecules between the $VOPO_4$ layers

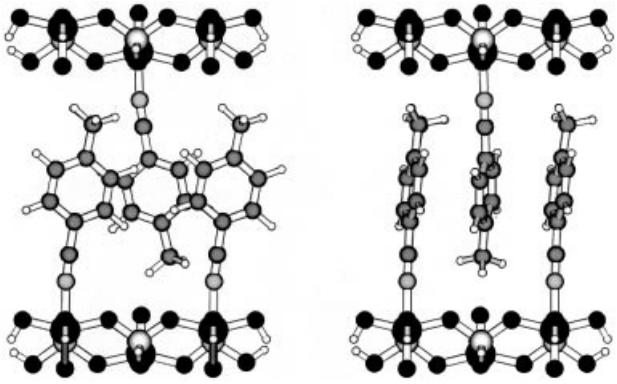

Figure 9. Side view of the PM3 optimized geometry of the molecular segment modeling the arrangement of *p*-tolunitrile molecules between the $VOPO_4$ layers

In the modeled structures one can observe cavities, which are larger for the tolunitrile intercalate than for the benzonitrile intercalate. The results of the model calculations indicate that water molecules, which are hydrogen-bonded to the oxygen atoms of the phosphate tetrahedron of the host layers, can be inserted into these cavities, in analogy with the second water molecules in vanadyl phosphate dihydrate.[14] Such water molecules can penetrate into the samples as soon as the latter are taken out of the ampoule. Amounts of incorporated water have been observed in the tolunitrile intercalate IR spectrum (as a Nujol suspension) at about 3500 and 3350 cm^{-1}, but they were not observed in the IR spectrum of the benzonitrile intercalate or of pure Nujol (see Figure 10). The overall (basic) crystalline structure of the intercalate is influenced by the presence of these water molecules only negligibly and thus the induced change is not observed in the diffractogram. However, the presence of the water molecules influences the coordination of the tolunitrile molecules in the vanadyl octahedron and

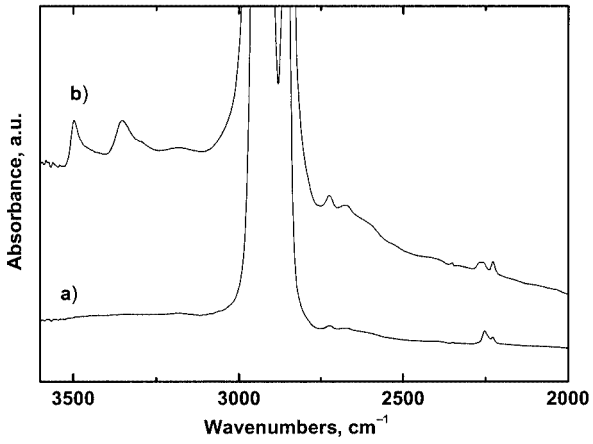

Figure 10. FTIR spectra of the benzonitrile (a) and tolunitrile (b) intercalates measured as a Nujol suspension

in the spectrum of the sample prepared as a Nujol suspension. This fact is probably shown by the presence of the second nitrile band at 2256 cm^{-1}, while the band at 2269 cm^{-1} corresponds to the original anhydrous tolunitrile intercalate structure. In the case of the KBr pellets we observe only a weak band of coordinated nitrile molecules in the hydrous intercalate, due to the decomposition of the sample by hydration during milling.

Conclusion

In contrast to aliphatic nitriles, molecules of aromatic nitriles are oriented perpendicularly to the host layers. The guest molecules are arranged in the interlayer space in an interdigitated manner, with the planes of the aromatic rings being parallel. This arrangement forms cavities between the guest molecules, especially in the *p*-tolunitrile intercalate. These cavities facilitate the incorporation of water molecules into the intercalates and thus reduce their stability. The assumption of the perpendicular arrangement of the guest molecules is supported by the fact that the basal spacing of the *p*-tolunitrile intercalate is about 2 Å higher than that of the benzonitrile intercalate. Quantum chemical calculations support the results of the IR and Raman spectroscopy indicating the formation of the C≡N→V donor-acceptor bond in the intercalates.

Experimental Section

Preparation: The intercalation compounds were obtained by a displacement reaction. The solid 2-propanol intercalate[10] was prepared in advance and used as a starting material for the reaction with the corresponding aromatic nitrile. The 2-propanol intercalate (0.5 g) was suspended in 10 mL of benzonitrile or molten *p*-tolunitrile and heated in a microwave field for 10 min. The samples were washed with toluene, dried in vacuo, and stored in a sealed evacuated ampoule.

XRD: Powder data were obtained with a D8 Advance X-ray diffractometer (Bruker AXS, Germany) using Cu-K_α radiation with a graphite secondary monochromator. Diffraction angles were measured from 5 to 50° (2θ). The samples were kept under a protection foil during the measurements and the signal of this foil in the diffractograms was compensated.

Thermogravimetry: The TG analyses were performed using a Derivatograph C (MOM Budapest, Hungary). The measurements were carried out in air between 20 and 700°C at a heating rate of 5 $K \cdot min^{-1}$.

IR Spectral Measurements: IR spectra in the range 400−4000 cm^{-1} were measured with a fully computerized Nicolet IMPACT 400 FTIR spectrometer (300 scans per spectrum at 2 cm^{-1} resolution). Measurements were performed in the transmission mode on a KBr pellet and a Nujol suspension for the intercalates and by the ATR technique on a ZnSe crystal for pure liquid guest-molecules. The spectra were corrected for the H_2O and CO_2 content in the optical path.

Raman Spectral Measurements: FT Raman spectra were collected using a Fourier transform near-infrared (FT-NIR) spectrometer Equinox 55/S (Bruker) equipped with FT Raman module FRA 106/S (Bruker) (128 interferograms were co-added per spectrum in the range 4000 to −1000 cm^{-1} at 4 cm^{-1} resolution).

Modeling: The strategy of the modeling was based on the quantum chemical geometry optimization of model compounds representing local structures and interactions appearing in the intercalates of vanadyl phosphate with nitriles. Quantum chemical calculations were carried out at the ab initio and semiempirical levels of theory employing the Gaussian 98[15] and MOPAC 2002[16] program packages, respectively. Local interactions and structures in intercalates of vanadyl phosphate with the nitrile group were studied at the DFT level using the B3LYP functional and 6-31G(d) basis set, geometrical optimization of larger structures including two vanadyl phosphate layers and five benzonitrile or *p*-tolunitrile molecules were performed at the semiempirical level using the PM3 method.

Acknowledgments

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